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The Journal
of the
SOCIETY OF DYERS AND COLOURISTS

Volume 70 Number 10

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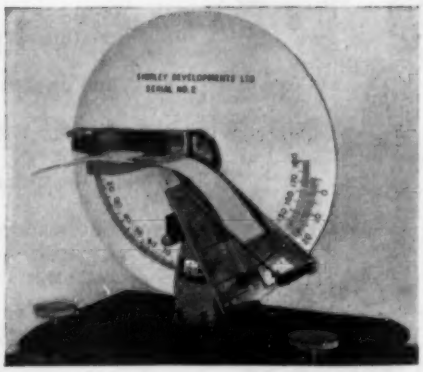

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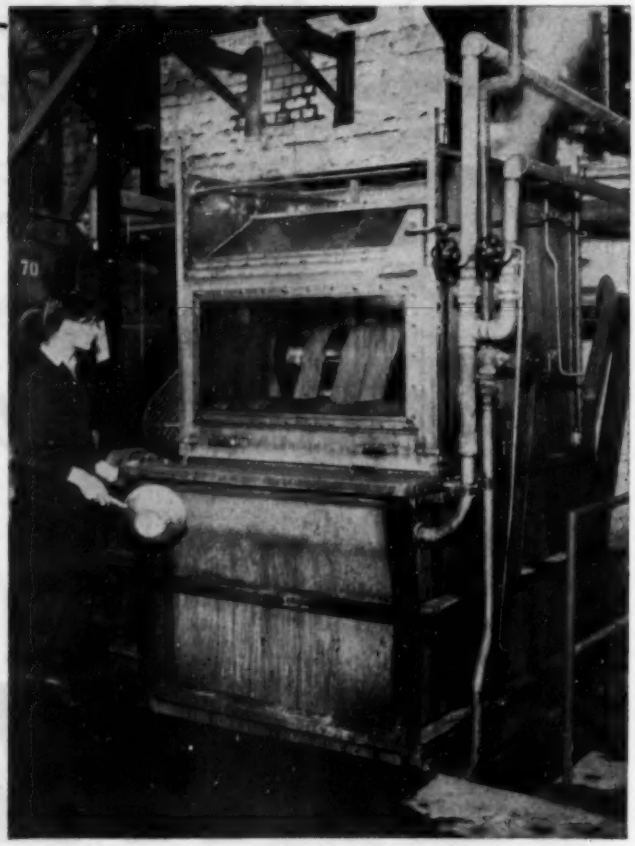

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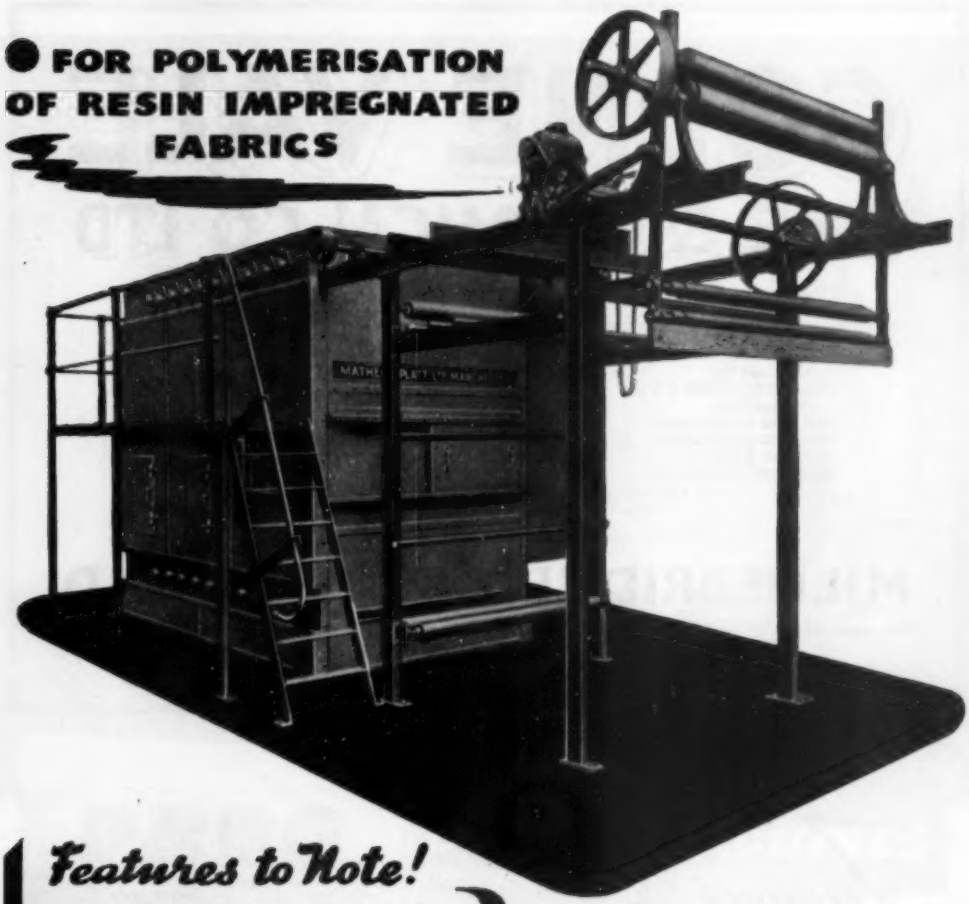

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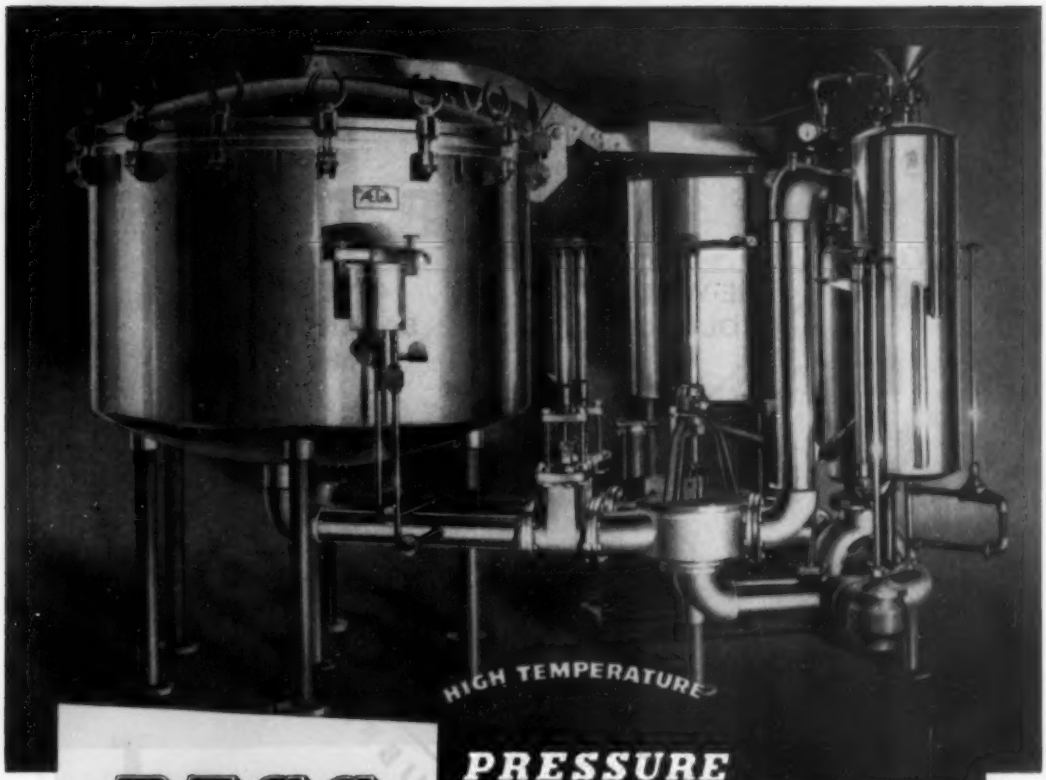

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NOTICE TO MEMBERS AND SUBSCRIBERS

Readers requiring *general information* regarding the Official Notices, List of Officers of the Society, etc. should consult pages 1–6 of the January 1954 and pages 262–266 of the July 1954 issues of the *Journal*, or write to *The Secretary*, The Society of Dyers and Colourists, Dean House, 19 Piccadilly, Bradford 1, Yorkshire (*Telephone* Bradford 25138–9). *Editorial Communications* should be addressed to *The Editor*, at the same address.

Forthcoming Papers

The following papers have been accepted by the Publications Committee, and will appear in future issues of the *Journal*—

LECTURES

Continuous Ribbon Dyeing	*L. J. Clarke*
The Dyeing of Felt	*D. Haigh*
Affinity Effects during Padding	*W. J. Marshall*
Some Applications of *iso*Cyanates	*G. S. J. White*

COMMUNICATIONS

The Polarography of Azo Dyes	*J. de O. Cabral and H. A. Turner*
Researches upon the Light Fading of Dyes— II	*H. R. Chipalkatti, C. H. Giles, et al.*
Qualitative and Quantitative Analysis of Vat Dyes by Paper Chromatography	*E. Klingsberg*
The Histology of Keratin Fibres	*B. Manogue, M. S. Moss, and R. L. Elliott*
Some Factors in the Measurement of Affinities of Vat Dyes for Cellulose	*R. H. Peters and J. Simons*

F.T.C.C. PUBLICATION

The Use of Fading Lamps for Determining Light Fastness	*K. McLaren*

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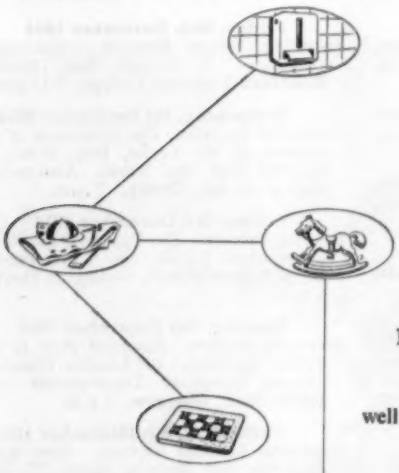

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FORTHCOMING MEETINGS OF THE SOCIETY

Monday, 25th October 1954

BRADFORD JUNIOR BRANCH. *Natural Colouring Matters.* A. N. Hay, Esq., **Bradford** Technical College. 7.15 p.m.

Thursday, 28th October 1954

WEST RIDING SECTION. *Incidents during 43 years Research.* Dr. H. H. Hodgson, Victoria Hotel, Bridge Street, **Bradford**. 7.30 p.m.

MIDLANDS SECTION. Discussion on *Dyeing Machine Design.* Opening Speaker — F. H. Marsh, Esq., B.Sc., F.R.I.C. Gas Theatre, **Nottingham.** 7 p.m.

Friday, 29th October 1954

HUDDERSFIELD SECTION. Annual Dinner in Princess Cafe, **Huddersfield.**

Friday, 5th November 1954

LONDON SECTION. *Fabric Faults and Unserviceable Accessories.* J. H. Moulder, Esq., B.Sc. (Assistant Director of the Dyers and Cleaners Research Organisation). Joint meeting with the Guild of Dyers and Cleaners (London Centre). Royal Society Rooms, Burlington House, **London W.1.** 6 p.m.

Tuesday, 9th November 1954

BRADFORD JUNIOR BRANCH. *Problems of the Garment Dyer and Finisher.* L. D. Broadbent, Esq. (Messrs. Sketchly Ltd., Hinckley). **Bradford** Technical College. 7.15 p.m.

Wednesday, 10th November 1954

NORTHERN IRELAND SECTION. *Some Observations on American Bleaching and Dyeing Processes.* J. K. Skelly, Esq. (Belfast College of Technology). Thompson's Restaurant, Donegall Place, **Belfast.** 7.30 p.m.

Thursday, 11th November 1954

WEST RIDING SECTION. *The Dyeing of Leather.* D. Woodroffe, Esq., M.Sc., A.R.I.C. (Head of Leather Department, Northampton College of Technology). Hotel Metropole, **Leeds**. 7.30 p.m.

Friday, 12th November 1954

MANCHESTER SECTION. Ladies' Evening. Visit to the Dyehouse Laboratories of I.C.I. Ltd. Full details later.

Tuesday, 16th November 1954

HUDDERSFIELD SECTION. *Classification of Dyestuffs by their Dyeing Characteristics.* W. Beal, Esq. (The Geigy Co. Ltd.). Co-operative Society Cafe, Buxton Road, **Huddersfield.** 7.30 p.m.

SCOTTISH SECTION. *Silicones in the Textile Industry.* T. W. Watson, Esq., B.Sc. (Midland Silicones Ltd.). St. Enoch Hotel, **Glasgow.** 7 p.m.

Wednesday, 17th November 1954

MIDLANDS SECTION. *Dyeing of Terylene above* 100°C. A. S. Fern, Esq., B.Sc., F.S.D.C. Kings Head Hotel, **Loughborough.** 7 p.m.

Friday, 19th November 1954

MIDLANDS SECTION. *Colour fastness from the point of view of the Manufacturer, Dyer and Consumer* (Forum) (Joint meeting with the Leicester Textile Society and Textile Institute). College of Technology, **Leicester.** 7 p.m.

Saturday, 20th November 1954

MIDLANDS SECTION. LADIES EVENING—DINNER DANCE. Black Boy Hotel, **Nottingham.** 7 p.m.

Monday, 22nd November 1954

HUDDERSFIELD SECTION. *Chemistry in the Woollen Industry.* J. Barritt, Esq., B.Sc., A.R.C.S., A.R.I.C., F.S.D.C. (Wool Industries Research Association). Joint meeting with Huddersfield Textile Society in the Large Hall, Technical College, **Huddersfield.** 7.30 p.m.

Thursday, 25th November 1954

WEST RIDING SECTION. *The Fixation of Direct Dyestuffs.* Dr. R. Gill (Allied Colloids Ltd.). Victoria Hotel, Bridge Street, **Bradford**. 7.30 p.m.

Friday, 26th November 1954

BRADFORD JUNIOR BRANCH. *Colorimetry and Match Prediction.* E. Cowgill, Esq. (Messrs. I.C.I. Ltd.). **Bradford** Technical College. 7.15 p.m.

Wednesday, 1st December 1954

MIDLANDS SECTION. *The Evaluation of Optical Bleaching Agents.* G. G. Taylor, Esq., B.Sc., A.Inst.P. (Joint meeting with the British Association of Chemists). College of Art, **Derby.** 7 p.m.

Friday, 3rd December 1954

LONDON SECTION. *The Dyeing of Textile Fibres at Temperatures above* 100°C. Mr. J. A. Fowler (I.C.I. Ltd.). Royal Society Rooms, Burlington House, **London, W.1.** 6 p.m.

Tuesday, 7th December 1954

SCOTTISH SECTION. *Electrical Aids to Production in the Textile Industry.* L. Landon Goodman, Esq., B.Sc. (British Electrical Development Association). St. Enoch Hotel, **Glasgow.** 7 p.m.

Wednesday, 8th December 1954

NORTHERN IRELAND SECTION. *Some aspects of Design in Bleaching and Finishing Plant.* W. W. Spooner, Esq. (Spooner Dryer and Engineering Co. Ltd.). (Joint Meeting with Foremen Dyers' Guild). Thompson's Restaurant, Donegall Place, **Belfast.** 7.30 p.m.

Thursday, 9th December 1954

WEST RIDING SECTION. *Oriental Printing Methods and Prints.* R. Thornton, Esq., B.Sc. (I.C.I. Ltd.). Victoria Hotel, Bridge Street, **Bradford.** 7.30 p.m.

Thursday, 16th December 1954

BRADFORD JUNIOR BRANCH. *Special Finishes for Textiles and their Evaluation.* (Clayton Dyestuffs Co. Ltd.). **Bradford** Technical College. 7.15 p.m.

Friday, 17th December 1954

MANCHESTER SECTION. *The Wear Properties of Resin Treated Fabrics.* Dr. T. H. Morton. Textile Institute. 6.30 p.m.

Tuesday, 21st December 1954

HUDDERSFIELD SECTION. *Printing of Wool, including Production of Melange Effects.* J. A. Potter, Esq., F.S.D.C. (Clayton Dyestuffs Co. Ltd.). The Co-operative Society Cafe, Buxton Road, **Huddersfield.** 7.30 p.m.

Thursday, 6th January 1955

NORTHERN IRELAND SECTION. *The Modern Approach to Linen Bleaching and Finishing* I. M. Hill, Esq. (Milltown Bleaching Co. Ltd.) (Joint lecture with Textile Institute). Thompson's Restaurant, Donegall Place, **Belfast.** 7.30 p.m.

Friday, 7th January 1955

LONDON SECTION. *Cellulose Acetate and Water Repellency.* R. J. Mann, Esq., B.Sc. (British Celanese Ltd.). Royal Society Rooms, Burlington House, **London, W.1.** 6 p.m.

Tuesday, 11th January 1955

BRADFORD JUNIOR BRANCH. Lecture. Title to be announced later (Messrs. S. Pegg & Son Ltd., Leicester).

Wednesday, 12th January 1955

NORTHERN IRELAND SECTION. *Application and Evaluation of Optical Bleaching Agents.* Messrs. G. Taylor and A. V. Cole (Clayton Dyestuffs Co. Ltd.). Thompson's Restaurant, Donegall Place, **Belfast.** 7.30 p.m.

Tuesday, 18th January 1955

HUDDERSFIELD SECTION. *Observations on the Dyeing of Wool at High Temperatures.* H. Sagar, Esq., A.T.I. (Imperial Chemical Industries Ltd.). The Co-operative Society Cafe, Buxton Road, **Huddersfield.** 7.30 p.m.

Friday, 21st January 1955

MANCHESTER SECTION. Details later. Textile Institute. 6.30 p.m.

continued on page xxix

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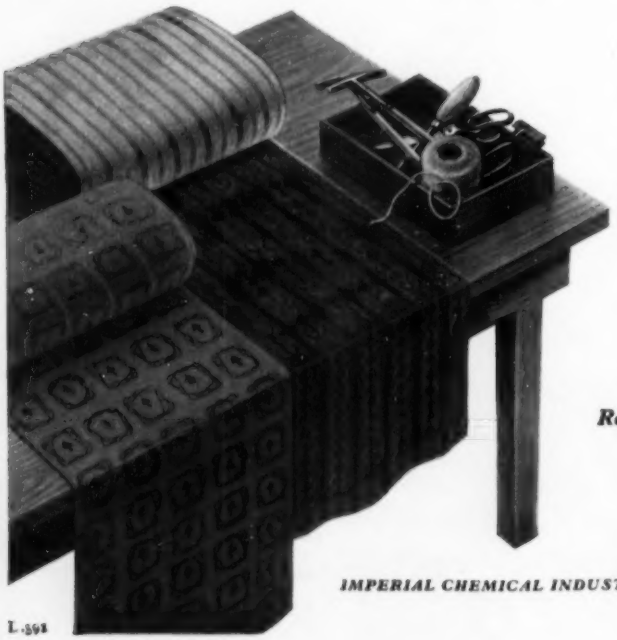

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THE JOURNAL

OF THE

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Volume 70 Number 10 OCTOBER 1954 *Issued Monthly*

Proceedings of the Society

Azoic Dyeing of Acetate Rayon

I. M. S. Walls

Meeting of the Manchester Junior Branch held at the College of Technology, Manchester, on 2nd November 1953, Mr. N. Hamer in the chair

The reasons why azoic dyes cannot be applied to acetate rayon by the technique used with cotton or viscose rayon are reviewed, and the "modified azoic" technique, in which the base and the coupling component are applied to the fibre in one bath and development is carried out *in situ* in a second bath, is described. A range of coupling components have been applied to acetate rayon from neutral and from weakly alkaline baths, the latter with and without common salt, and the uptakes have been measured. Similarly the exhaustions of diazo components have been determined. This information is used as a guide to the most suitable azoic components for acetate rayon, and to the conditions under which they should be applied. An investigation has been carried out into the ratio in which the coupling and diazo components should be mixed when they are applied to the fibre together, and the preferred diazotisation and coupling conditions have been determined. The factors involved in the soaping aftertreatment are discussed and the recommended soaping conditions are described. The light fastness assessments of a wide range of azoic combinations on bright acetate rayon are tabulated.

INTRODUCTION

The application of azoic dyes to acetate rayon does not represent a new method of colouring this fibre. It is more than twenty-five years since the first attempts were made to dye acetate rayon in this way, and since then several workers have published the results of their investigations. Among these may be mentioned Wallwork [1], Metzger and Röhling [2], Mellor and Olpin [3], and Carmichael and Ivey [4]. It has been made clear that azoic dyes cannot be applied to acetate rayon by the technique used for cotton or viscose rayon for two reasons—

(*a*) The coupling components cannot be applied from moderately strong alkaline solutions of their sodium salts owing to saponification of the fibre by solutions of such alkalinity at the dyeing temperatures required.

(*b*) The diazo components cannot be applied from cold solutions to the fibre impregnated with coupling component. In such solutions the acetate rayon is only slightly swollen, and its small pore size prevents adequate diffusion of the diazotised base into the fibre. If the temperature is raised to swell the fibre, the diazotised bases decompose.

The most popular technique which has been evolved to overcome these difficulties, sometimes called the *concurrent* or the "modified azoic" technique, consists in the simultaneous application of a coupling component and a diazo base by dyeing at 70–85°C., followed by diazotisation of the base *in situ* with consequent coupling, and a soaping aftertreatment.

In recent years there has been an increasing demand for colours of very good wet fastness on acetate rayon for such purposes as bathing-costume fabrics. In the past this demand was met sometimes by the use of azoics and sometimes by applying vat dyes, e.g. the Marchington process [5]. Since this demand has increased, it was considered that a systematic investigation into the application of azoic dyes to this fibre might well be undertaken, so that fuller information would be available on—

(1) The substantivity of different coupling and diazo components for the fibre

(2) The best method of applying them, and the proportions in which they should be used

(3) The most suitable conditions for the diazotisation and coupling reactions

(4) The aftersoaping reagents, and the times and the temperatures required for aftersoaping the different azoic combinations

(5) The fastness properties of a wide range of these combinations on acetate rayon.

APPLICATION OF COUPLING COMPONENTS

Although coupling components cannot be applied to acetate rayon from the alkaline solutions that are used for cotton or viscose rayon, there are two

alternative methods of application, the first consisting in dyeing as neutral or near neutral dispersions, while the second uses weakly alkaline solutions. These methods have been investigated, and the exhaustions of the different coupling components on to the fibre were measured for both methods.

It was found that neutral dispersions of the coupling components were most satisfactorily obtained by pasting the component with an equal weight of methanol, and adding caustic soda (as a 20% solution) equal to one-fifth of the weight of the coupling component, followed by a little warm water. This solution was added to a dyebath which contained Dispersol VL (1 g./litre). A quantity of sodium dihydrogen phosphate equal to eight times the weight of caustic soda present was than added in solution to the dyebath. This always gave a pH of ca. 7·3, and the coupling component was precipitated as a very fine dispersion. Dispersions of fifteen components were prepared in this way, and dyed on to 2-g. hanks of bright acetate rayon yarn (291-denier yarn, singles 12 t.p.in. Z, doubled 10 t.p.in. S) in 1% and 5% depths (on the weight of material) at 80°c. for 90 min. from a bath with a liquor ratio of 30 : 1. Four coupling components were also dyed in 5% depths at 60°c. The hanks were rinsed twice in cold water, and the rinsings added to the dyebath, which was then made up to 250 ml. with methanol to dissolve the residual coupling component. After further appropriate dilution with methanol, the optical densities of the solutions were measured at previously determined absorption peaks in the ultraviolet region of the spectrum using the Uvispek (Hilger) spectrophotometer. The figures obtained were compared with the corresponding optical densities of standard solutions, and the percentage exhaustions of the dyebath were calculated (Table I).

Before the coupling components were applied from weakly alkaline solutions, it was necessary to ensure that objectionable hydrolysis of the fibre would not occur. The components are conveniently dissolved by the method adopted in the preparation of the neutral dispersions, and the quantity of caustic soda used there—one-fifth of the weight of component—is the minimum quantity that can be used with most coupling components if solution is to be complete. If such solutions, without subsequent neutralisation, are to be used to dye acetate rayon, it is important to make certain that their alkali content does not affect the fibre. The concentration of alkali present will vary according to the depth of dyeing and the liquor ratio employed, hydrolysis of the fibre being most likely in heavy depths dyed in short liquors. Pieces of bright acetate rayon were therefore treated for 2 hr. at 80°c. (a longer period than the usual dyeing time, at the usual dyeing temperature) in, respectively, 0·2%, 0·04%, and 0·008% aqueous solutions of caustic soda flake. It was calculated that the alkalinity of these solutions ranged from that which might be present when a very heavy dyeing is applied from a very short liquor to that found when a medium depth is dyed at a medium liquor ratio. After being rinsed, the alkali-treated materials were dyed with Chlorazol Sky Blue FF to estimate, roughly, the degree of saponification that had occurred. It was found that only the most strongly alkaline of the three solutions had caused any marked hydrolysis of the fibre, and even then it would be significant only if azoic-dyed material were to be subsequently cross-dyed. Remembering that, in practice, dyebaths are not likely to develop the alkalinity of the corresponding caustic soda solutions, owing to absorption of carbon dioxide from the air, it was concluded that it was quite safe to use the weakly alkaline dyebaths that were employed in the dyeings carried out in the work described here. When very heavy dyeings are applied at short liquor lengths, the precaution may be taken, if desired, of adding a small quantity of acetic acid to the dyebath to guard against the development of an unduly high pH, the alteration in percentage absorption caused by this addition being borne in mind.

The same fifteen coupling components were then dyed on to acetate rayon yarn from weakly alkaline solutions made up as described, both without salt and with salt (20 g./litre). The dyeing conditions were in other respects the same as those used in applying the neutral dispersions, but only 5% depths of the components were applied from the alkaline solutions, it not being considered necessary to dye the weaker depths in this way. The exhaustions of the dyebaths (Table I) were estimated spectrophotometrically as before, save that the dyebaths were carefully neutralised with hydrochloric acid before the methanol was added.

TABLE I

Absorption of Azoic Coupling Components by Acetate Rayon

(% Exhaustion)

(Dyed on bright acetate rayon yarn for 90 min. at 30 : 1 liquor ratio; Dispersol VL (1 g./litre) in dyebath)

Brenthol, on wt. of fibre ...	Dispersion (pH 7·3)			NaOH Soln.	NaOH + NaCl
	5%		1%	5%	5%
	60°c.	80°c.	80°c.	80°c.	80°c.
BT	—	62	87	64	84
FR	26	60	94	36	88
BC	—	42	75	33	87
AN	23	38	67	50	70
MA	—	30	76	40	40
OT	< 5	25	89	34	71
FO	—	23	92	38	37
AT	—	15	62	35	71
MN	—	15	74	24	17
AS	5	8	34	15	38
PA	—	5–10	40	16	13
BN	—	9	42	10	13
BA	—	10	21	—	16
BB	—	< 5	20	—	5
CT	—	< 5	8	—	8

Several points become clear from a survey of these results—

(1) Several coupling components have very little affinity for this fibre and should not be

used. These include Brenthols CT, BB, and BA (which incidentally contain bromo or chloro substituent groups).

(2) Several coupling components have a reasonable exhaustion in depths up to medium, but this falls off rapidly in heavier depths. These include Brenthols BN, PA, AS, and MN.

(3) The remainder possess quite a high affinity for the fibre and build up at least adequately, and in some cases very well. These preferred coupling components are Brenthols BT, FR, BC, AN, MA, OT, FO, and AT.

(4) The exhaustion of the coupling components is usually higher from weakly alkaline solutions, and is nearly always improved by the addition of common salt.

(5) In the four cases examined, the absorption of coupling components is reduced by a fall in the dyeing temperature.

The rates of dyeing of three coupling components in 5% depths were measured using both neutral dispersions, and also weakly alkaline solutions containing salt (20 g./litre), the curves being shown in Fig. 1 and 2. It can be seen that a reasonable exhaustion can be obtained in 60 min. even with these heavy depths, but this can sometimes be improved, and better penetration obtained, if the dyeing is prolonged by a further 30 or 60 min.

From the results in this section, eight coupling components can be recommended for application to acetate rayon. They should be applied at 80°C. from the weakly alkaline solutions that result from dissolving the coupling component with one-fifth of its weight of caustic soda, using common salt (10–20 g./litre) in the dyebath.

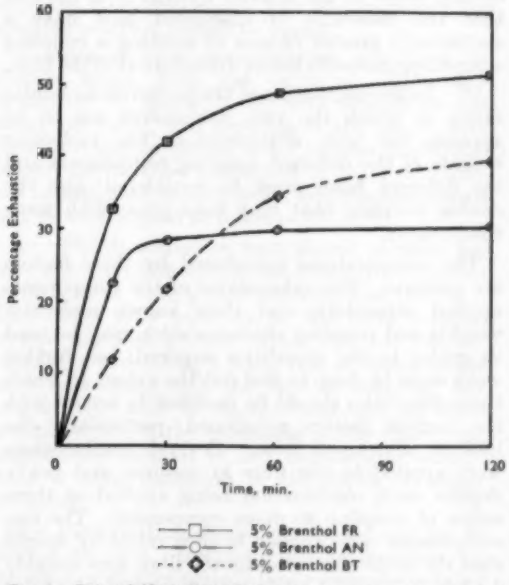

FIG. 1— Rate of Absorption of Coupling Components from Neutral Dispersions at 80°C.

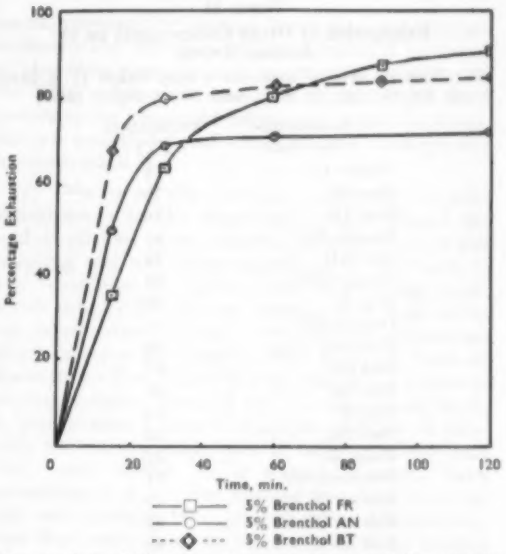

FIG. 2— Rate of Absorption of Coupling Components from slightly Alkaline Solution in the presence of Common Salt at 80°C.

APPLICATION OF DIAZO COMPONENTS

In studying the application of diazo components to acetate rayon the first problem was to obtain satisfactory dispersions in the dyebath. Several dispersing agents were tried, and it was eventually found that the best method was to paste the bases with soap flakes and a little water, add hot water, and boil for a few minutes. Good-quality bases, free from tarry residues, must, of course, be used. Many of the bases dissolve on such treatment, although they precipitate out on cooling. If hot solutions of the bases are added to a warm dyebath, the dilution that occurs is sufficient to keep some of them in solution, and most of the rest give satisfactory dispersions. Certain diazo components marketed as the water-soluble hydrochlorides (e.g. Brentamine Fast Orange GC Base and Brentamine Fast Red KB Base) were neutralised with caustic soda in the dyebath in the presence of soap, giving dispersions of the free bases.

The rates of dyeing of three diazo components were measured using dispersions prepared in this way (exhaustions were determined by the technique described below). It can be seen (Fig. 3) that the bases dye much more quickly than the coupling components, and that the exhaustion is only slightly improved if a dyeing time longer than 60 min. is used. Since this is a convenient dyeing time, the uptake of the various bases by bright acetate rayon was measured by dyeing them in 5% depths (on the weight of material) on 2-g. hanks, at a 30 : 1 liquor ratio, at 80°C. for 60 min. The exhaustion (Table II) was measured by adding 25 ml. of concentrated hydrochloric acid and 25 ml. of 25% potassium bromide to the exhausted dyebath, diluting to 500 ml., and titrating the whole against 0·02 M. sodium nitrite, using starch–iodide solution as an external indicator. It is interesting to

TABLE II

Exhaustion of Diazo Components on to Acetate Rayon

(5% Base on wt. of material + soap flakes (1 g./litre) Dyed for 60 min. at 80°c. and 30 : 1 liquor ratio)

Brentamine Fast Base	Exhaustion (%)
Yellow GC	78
Blue 2B	78
Red TR	76
Scarlet 2G	75
Red KB	74
Garnet GBC... ...	73
Blue B	72
Orange GC	70
Red 3GL	68
Red GL	67
Red RC	66
Red B	54
Red RL	53
Violet B	53
Bordeaux GP ...	51
Scarlet G	49
Scarlet RC	49
Red LTR	49
Orange GR	43
Red 2G	30

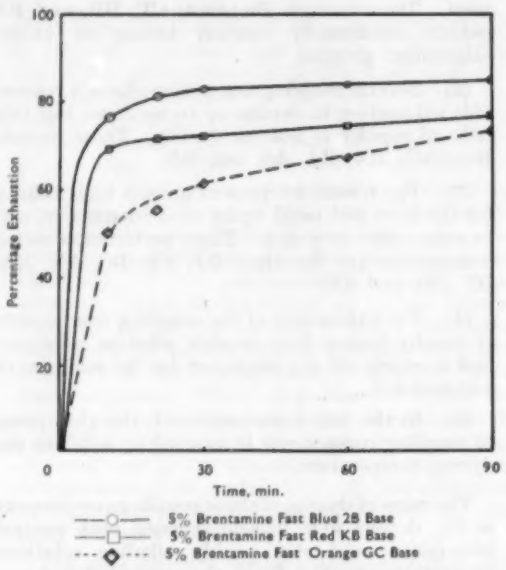

FIG. 3—Rate of Absorption of Diazo Components at 80°c.

observe that the order in which the bases are found in Table II is in general similar to the order of their exhaustions on to nylon [6] and Terylene polyester fibre [7]. The figures for acetate rayon show that nearly all the bases can be used satisfactorily on this fibre. It was not considered necessary to measure the exhaustions for a lower depth, since these will be either similar to or higher than the values in Table II.

SIMULTANEOUS APPLICATION OF COUPLING COMPONENT AND DIAZO COMPONENT

The data so far obtained permitted selection of the most suitable coupling components for this work and showed that nearly all the diazo components can be used. The coupling and diazo components can be prepared separately by the methods outlined in the preceding two sections, and their concurrent application presents no difficulties. However, the ratio or ratios of coupling to diazo components which should be used for different combinations at different depths of dyeing must be decided upon, and in connection with this several factors must be considered—

(*a*) The exhaustions of the various coupling and diazo components on to the fibre, measured when they are applied individually, may be appreciably modified if they are applied together. For example, one of the components may have a swelling action on the fibre, and may increase the rate of dyeing and the uptake of the other; alternatively, one of the components may exert some sort of blocking action, perhaps through competition for sites on the fibre surface, thus reducing the uptake of the other.

(*b*) When the two components have been applied to the fibre, the base is diazotised *in situ*, and the molecules of diazonium salt will then migrate in the fibre until they meet and couple with molecules of the coupling component. If this reaction does not occur, they diffuse out of the fibre into the diazotisation bath. This wastage of base takes place to a considerable extent, as can be demonstrated by adding the sodium salt of a coupling component to the diazotisation bath after the fibre has been removed, when appreciable quantities of pigment are formed. Consequently a considerable excess of base should be present in the fibre before diazotisation takes place. The extent of this excess will vary with the depth of dyeing, since in the heavier dyeings it is obvious that the molecules of diazotised base have a statistically greater chance of meeting a coupling component molecule before diffusing out of the fibre.

(*c*) In the calculation of the preferred molecular ratios in which the two components are to be applied, the wide differences in the molecular weights of the different coupling components and the different bases must be considered; also the double coupling that may take place with some components.

The complications introduced by these factors are obvious. The exhaustions of the components applied separately, and their known molecular weights and coupling characteristics, may be used as guides to the quantities required; but further work must be done to find out the extent to which these quantities should be modified to accord with the various factors mentioned, particularly the loss of diazotised base. Several combinations were applied to the fibre in medium and heavy depths, each combination being applied at three ratios of coupling to diazo component. The two components were applied in such ratios by weight that the molecular ratios on the fibre were roughly 1 : 1·5, 1 : 2, and 1 : 3 (coupling component : base) respectively. A wide range of combinations were

applied at the two depths with the above ratios of the components, developed, and soaped. It was found that, in general, the intermediate ratio was to be preferred for medium depths, but for the heavy depths the 50% molecular excess of base was frequently sufficient. Using less than the preferred quantities of base caused a marked decrease in the depth of colour produced, while higher quantities caused only a small increase.

From these preferred molecular ratios the approximate proportions by weight in which the individual components should be used in any desired combination were calculated, and dyeing recipes which conformed to these were used in the final dyeings carried out for fastness tests. A point that may be emphasised here is that an unnecessarily large excess of base is usually preferable to an excess of coupling component, since most uncoupled diazotised base will diffuse out of the fibre during the diazotisation and coupling stage, while uncoupled coupling component will tend to remain in the fibre and dull the final colour. A large excess of base must, of course, be avoided with highly coloured bases such as Brentamine Fast Garnet GBC.

DIAZOTISATION AND COUPLING

After the coupling and diazo components have been applied to the fibre, diazotisation is carried out in a separate bath containing sodium nitrite and an acid. With most combinations, coupling can be completed in the same bath. The following points had to be considered here—

(*a*) The quantities of sodium nitrite and acid required, and selection of acid

(*b*) Temperature and time of diazotisation

(*c*) Certain combinations do not couple satisfactorily in the diazotisation bath, and in these cases the most convenient way of completing the coupling reaction had to be found.

A series of azoic combinations was dyed on acetate rayon satin (34 oz./sq.yd., 213 warp threads of 73 denier × 71 weft threads of 140 denier per inch), and portions of the pieces were diazotised and developed under various conditions. One of the variables mentioned in (*a*) or (*b*) above was investigated in each series, and the conclusions may be summarised as follows—

(*a*) The diazotisation bath should contain, per litre, 3–5 g. sodium nitrite and either 5–8 g. glacial acetic acid or 6–10 g. hydrochloric acid (32°Tw.). Acetic acid may seem to be the more rational acid to use with acetate rayon, and has the advantage of promoting a lower rate of diazotisation more in keeping with the rate of coupling, but hydrochloric acid is cheaper and can be used satisfactorily. If the quantities of the diazotising reagents are reduced to any considerable extent, there is some reduction in the depth of colour produced.

(*b*) Diazotisation should be carried out for 30 min. at 20–25°C. Increasing the temperature for the same or shorter periods tends to produce duller colours, possibly owing to some nitrosation of the coupling components. Sometimes weaker shades result, presumably because the higher temperature increases the diffusion of the diazotised base out of the fibre more than it accelerates coupling in the fibre. In some cases 30 min. is longer than necessary for even cold diazotisation and coupling, but it is considered that this time is the best general recommendation.

(*c*) Nearly all the combinations tested coupled satisfactorily in the diazotisation bath, under the acid conditions present there. In any event, if the coupling was not quite completed in this bath, it was completed in the neutral aftersoaping bath, which usually follows the diazotisation stage without intermediate drying. However, combinations which involve Brentamine Fast Blue 2B Base or Brentamine Fast Violet B Base would not couple to any appreciable extent in the acid diazotising bath. It was necessary here to diazotise cold for 15 min. with the normal quantities of sodium nitrite and acid, and couple in a second, neutral bath containing 2 g. sodium acetate per litre, starting cold and raising to 60°C. over 15 min. Aftersoaping was then carried out in the same bath by adding the necessary soaping agents and raising the temperature further to 90–95°C.

SOAPING

It is well known that azoic dyeings (and vat dyeings) on cotton or viscose rayon require a soaping aftertreatment to remove loose surface pigment and produce their true colours, the resulting dyeings usually having higher light fastness than the unsoaped ones. Reference may be made to the work of Bean and Rowe [8,9], Kornreich [10], Wegmann [11], and Sumner, Vickerstaff, and Waters [12], among others. During soaping the fibre swells and the individual pigment molecules migrate until they become joined together in aggregates. If the treatment is prolonged, migration continues, presumably until the aggregates are too large for further movement. Before this condition is achieved, however, a considerable proportion of the smaller aggregates migrate to the fibre surface, or, in cotton, to the lumen. In cotton this produces poor rubbing fastness, and in viscose or acetate rayon poor rubbing fastness together with some "blinding" (loss of lustre) of the fibres. The desirable colour change and improvement in light fastness are associated with the earlier stage of the soaping treatment, namely the initial stages of aggregation. It is impossible to separate rigidly the process into two stages, aggregation and migration, but it is convenient to consider it as occurring in these two stages, and to assume that aggregation takes place first and represents the joining together of individual molecules into clusters, while migration occurs subsequently and represents the movement of small aggregates (or even individual molecules) towards the surface. Using these terms, the ideal aftersoaping treatment would promote the desired aggregation with the concomitant colour change and improved light fastness, but would keep the subsequent undesirable migration stage to a minimum. This simplified picture must not be interpreted too rigidly, since the mechanism of

aggregation is still not clearly understood. It has been described as a process of crystallisation, but the actual form of the larger particles is not under consideration here.

If the best soaping conditions are to be achieved, three variables must be considered, viz. the soaping agent, the temperature, and the time. Various agents, including soap and certain anionic and non-ionic agents, both with and without soda ash and with and without common salt, were examined. The most satisfactory combination was Lissapol NC (1 g./litre) and salt (5 g./litre). The addition of soda ash gave slightly improved results, but it is not considered that this alkali should be used at the high soaping temperatures required. The addition of common salt assists in preservation of the lustre of the fibre.

The critical factor in the aftersoaping treatment is the temperature, and this varies with the azoic combination. In most cases it is found that soaping for, say, one hour at a temperature a few degrees below a critical temperature will bring about only a small part of the required colour change produced by 10–15 min. soaping at a few degrees above this critical figure. It is important, therefore, to know the region of this critical temperature for each combination, and to soap at a slightly higher temperature for a period which is long enough to complete the colour change but not long enough to encourage extensive migration to the surface. If the temperature is much higher than the critical value, this migration to the surface will take place in a comparatively short time. Besides being unnecessary, it would have taken too long to determine the critical temperature at all accurately for each combination, and accordingly two temperatures—80°C. and 90°C.—were selected as providing a satisfactory alternative. Soaping was carried out for all the combinations used at both temperatures, and for periods of 15 min. and 30 min. (and 60 min. for some combinations), the colour change noted, and the rubbing fastness assessed. The majority of the combinations had a critical soaping temperature between 80°C. and 90°C. and required soaping at 90°C.; but for an important minority, mainly oranges and scarlets, this critical temperature was below 80°C., and these must be soaped at 80°C. if blinding is to be avoided. These latter combinations are indicated in Table III, which shows also those combinations which are prone to blinding, even at the recommended temperatures, if soaping is carried on too long. It was found that, under laboratory conditions, 15 min. soaping at the preferred temperature was usually sufficient to complete the required aggregation stage, although on a bulk scale this may need to be increased slightly. Combinations including Brenthol BT, Brentamine Fast Blue 2B Base, or Brentamine Fast Violet B Base require soaping for rather longer than the usual period if the aggregation stage is to be completed. It is recommended that such combinations be soaped for at least 30 min. at 90–95°C. The lustre of the material is not impaired at this temperature if common salt and Lissapol NC are employed, but care should be exercised with certain types of fabric because of the thermoplasticity of acetate rayon. It may be mentioned here that aggregation is not necessarily carried as far in acetate rayon as in cotton.

If the correct soaping conditions are used, it is nearly always possible to produce a finished article with a rubbing fastness that is at least satisfactory and sometimes excellent. Normally those combinations which have been noted as being prone to blinding will be avoided, since they will also tend to have poor rubbing fastness, but with the wide choice of combinations available this is no great handicap.

FASTNESS PROPERTIES

Different combinations (106) of coupling components and diazo components were selected from colour and light fastness considerations, their properties on viscose rayon and cotton being used as a guide. These combinations were dyed on acetate rayon satin, use being made of the previously determined data on the coupling

TABLE III

Soaping Temperature and Daylight Fastness of Azoic Combinations on Bright Acetate Rayon

(Medium depths. Soaping at 90°C., unless 80°C. indicated by asterisk)

Brentamine Fast Bases	AN	AS	AT	BC	Brenthols BT	FO	FR	MA	OT	PA
Yellow GC ...	—	—	—	4†	6	—	—	4*	4–5‡	4*
Orange GC ...	3–4*	—	—	4–5†	6–7	5*	4–5*	4–5*	3–4*	4*
Orange GR ...	6–7	4–5*	3	—	6–7	6–7	6	—	6	—
Scarlet G ...	5–6	—	3	—	6–7	5–6‡	5–6	5‡	5–6	4–5*
Scarlet RC ...	—	—	—	4*‡	—	5–6‡	5‡	5–6‡	4–5*	4*
Scarlet 2G ...	6	—	4–5	—	6	6–7	6	5	5	4*
Red KB ...	4–5	—	5	—	6	6–7	6	—	4–5	4*
Red B ...	6–7	—	5–6	—	6–7	6	6–7	6	6–7	4–5
Red RL ...	6	—	5–6	—	7	6–7	—	—	—	5–6
Red 2G ...	4–5	—	3–4	—	7	5–6	6‡	6	6*	5–6*
Red LTR ...	4–5	—	2	—	6–7	5–6	5	4–5	4	6
Red GL ...	6–7	—	4	—	6–7	6	5–6	—	6	6–7
Bordeaux GP ...	4–5	—	—	3	—	3–4	3–4	3–4	—	3
Violet B ...	2	1	—	2	—	—	1	3	3	2
Blue 2B ...	3	3–4	—	3–4	—	3	4	3–4	4	3

* Soaping at 80°C. † Severe blinding ‡ Tendency to blinding if soaping time is prolonged

component : base ratio and the aftersoaping conditions. The wet fastness properties were uniformly good, and the light fastness assessments of the different combinations are included in Table III.

CONCLUSIONS

The present work has shown that a very wide range of azoic dyes are eminently suitable for application to acetate rayon. They have highly satisfactory fastness properties on this fibre, and their application is by no means difficult. The range of colours that can be produced is very wide, and some of them, e.g. certain scarlets, are of a brightness that cannot readily be achieved with disperse dyes.

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Discussion

Dr. W. SHAW: Table I shows a decrease in temperature to have a marked effect on the absorption of dispersed coupling components. Is this true when they are dyed from alkaline solution, and is it operative also in the case of the dispersed bases?

Dr. WALLS: From the rate-of-dyeing curves of both the coupling components and the bases (Fig. 1–3) it can be seen that an equilibrium exhaustion is not usually achieved in the normal dyeing time even at 80°C. Any reduction in the dyeing temperature will reduce the rate of dyeing and consequently the uptake of either component. A swelling effect by either component when they are applied together may tend to counteract this effect.

Dr. SHAW: Does this marked temperature effect adversely affect the jig dyeing of piece goods?

Dr. WALLS: Practical experience has shown that level results are very easily obtained on the jig, and no complaints have arisen on this count.

Mr. B. KRAMRISCH: The process has been stated to be of special interest for acetate rayon bathing costumes, from which it can be assumed that the dyes are fast to chlorine. Is it possible to dye solid shades on acetate–viscose rayon mixtures which may be used for bathing costume material, and does the presence of lastex yarn interfere in any way?

Dr. WALLS: Solid shades can be dyed on acetate–viscose rayon mixtures with azoics. The coupling component is applied to both fibres from the first bath, which contains also enough free base for the acetate rayon portion of the material. This base is diazotised *in situ* and coupled with the coupling component on the acetate rayon, while the coupling component on the viscose rayon is coupled with a diazo component usually applied in a separate bath. The difficulties that arise are due to the difficulty of apportioning the coupling component equally between the acetate and viscose rayon fibres. The acetate rayon is usually dyed first at 60–80°C. for 20–30 min., and the temperature then lowered to 30–40°C. to increase the absorption of coupling component by the viscose rayon. The best conditions will depend on the combination and the depth of dyeing, and will be found by experience.

Fabrics incorporating lastex yarn have been dyed very satisfactorily with azoics.

Mr. KRAMRISCH: Acetate rayon is dyed in certain instances in staple form for blending with dyed wool. As the latter is normally dyed in colours of high wet fastness with e.g. chrome dyes, will acetate rayon dyed with azoic dyes withstand the necessary wet treatments such as alkaline milling, potting, and acid cross-dyeing with acetic and sulphuric acids?

Dr. WALLS: In general it may be said that azoic-dyed acetate rayon will withstand the wet treatments given to wool, provided that the fibre itself is not affected by the treatment. Alkaline milling and acid cross-dyeing do not affect the azoic dyeings.

Mr. S. BURGESS: Do some diazo components give trouble by tarring in the dyebath?

Dr. WALLS: Some of the diazo components marketed as hydrochlorides, and neutralised to the free bases in the dyebath, tend to form oils owing to their low melting points. If their concentration in the dyebath is not too high, they will remain in solution, and consequently it is recommended that, for heavy dyeings in short liquor lengths, these bases be added to the dyebath in portions during the first 30 min. of the dyeing time.

Mr. BURGESS: Are combination shades possible: can two coupling components be applied with one diazo component or one coupling component with two diazo components?

Dr. WALLS: Yes, provided that the rates of coupling of, for example, the two bases used are of the same order. Such a technique is rarely necessary, however, since such a large number of combinations are available. At the worst, only very slight shading should be necessary.

Mr. F. CROMPTON: Are the yellows obtained with Brenthol AT satisfactory?

Dr. WALLS: Bright yellows of quite good light fastness are obtained using Brenthol AT and, preferably, Brentamine Fast Red KB Base. Similarly, golden yellows can be obtained with Brentamine Fast Red B Base or Brentamine Fast Red RL Base.

Mr. CROMPTON: Does formic acid in the diazotisation bath give any superior result?

DR. WALLS: For those combinations with which it was tested, formic acid offered no advantage over acetic or hydrochloric acid.

Mr. E. E. BOWKER: When disperse dyes are applied to titania-delustred acetate rayon, there is normally a drop in light fastness. Is a similar result obtained with azoic dyes?

DR. WALLS: In general, the light fastness of azoic dyes on delustred acetate rayon is lower than on the lustrous material.

Mr. BOWKER: What is the resistance of the blue components to gas-fume fading?

DR. WALLS: The blue azoic dyeings are not subject to gas-fume fading.

Mr. BOWKER: Have any experiments been carried out using organic bases in place of caustic alkali?

DR. WALLS: Only very few; these indicated that, under the conditions used, organic bases did not offer any worthwhile advantage.

Mr. H. HEMPLING: Are all azoics besides the combinations using Blue 2B Base immune from gas-fume fading, e.g. the browns?

DR. WALLS: Yes.

Mr. J. GREENWOOD: In package dyeing does any filtration of the dispersed bases take place?

DR. WALLS: The condition of the dispersed bases varies, but a number of them are soluble in dyebath concentration at the dyeing temperature. We have carried out some package dyeings and obtained satisfactorily level results, but the state of the dispersion varies not only with the base but with the thoroughness with which it has been prepared before addition to the dyebath.

Mr. GREENWOOD: Has any alcohol other than methyl alcohol been used?

DR. WALLS: Industrial spirit is the cheapest alcohol to use in preparing a solution of the coupling component, and since it is perfectly satisfactory for this purpose it would seem to be the best recommendation for bulk usage.

COMMUNICATIONS

The Combination of Wool with Acids

L. PETERS

Conclusions drawn from experiments on the combination of keratin with mixtures of sulphuric and hydrochloric acids [1,2] are criticised. Inconsistencies in the data are corrected, and the results recalculated on this basis.

It is shown that the statistical test employed cannot be used to decide between rival theories, and the exact meaning to be attached to t-values is illustrated by an example.

A critical examination is made of the assumptions which have to be made to test the Donnan and Gilbert–Rideal theories, and the claim that these data favour the latter is rejected.

A previous issue of the *Journal* contains an article by B. Olofsson on the combination of wool keratin with mixtures of hydrochloric and sulphuric acids [1]. In the paper it is asserted that the data, and statistical calculations based on them, confirm the applicability of the Gilbert–Rideal theory [2] and disprove the Donnan treatment applied by Peters and Speakman [3]. This assertion, however, appears to be incorrect, since a different conclusion follows from a more rigorous analysis of the data and a proper interpretation of the meaning of the statistical parameters. This article aims to discuss not the relative merits of the two theories, but only the abovementioned attempt to discriminate between them.

CRITICISM OF THE ACCURACY OF THE DATA

In Olofsson's experiments, wool samples were left to come to equilibrium with mixtures of acids, but when the values for the hydrogen ion concentration c_{H^+} remaining in solution are compared with those of the chlorideion concentration c_{Cl^-} where sulphuric acid is absent [1] (*loc. cit.*, Table I, p. 507) the estimations are found to be inaccurate; whereas c_H and c_{Cl} should be identical, the values in the very first example in the Table are 1·6 and 0·1 millimoles/litre respectively. Other pairs of values which should be identical are— 3·7 and 0·8, 5·0 and 4·6, 10·2 and 10·7, 24·3 and 25·7, and 48·5 and 45·6 millimoles/litre. It is true that these particular data are not used in the further calculations, but they illustrate the errors which must be present in the other cases. It is most probably the method of titration of the chloride that is the cause of this error, for the discrepancies in the data for sulphuric acid in the absence of hydrochloric acid are much smaller: pairs of values for c_H and $2c_{SO_4}$ which should be equal are—0·9 and 0·4, 1·6 and 1·2, 2·5 and 2·0, 6·6 and 6·6, 19·6 and 20·4, and 42·0 and 42·4 milliequivalents/litre respectively. When both chloride and sulphate are present, similar discrepancies occur. Olofsson himself admits that his concentrations do not agree stoichiometrically, but believes the magnitude of these errors to be negligible. The following analysis, however, will show this belief to be erroneous.

INCOMPLETE IONISATION OF SULPHURIC ACID

A far greater source of error, however, is the neglect of incomplete ionisation of the sulphuric acid. Olofsson recognises this, but claims that taking it into account does not give better agreement between theory and experimental values. The second dissociation constant K_2 of sulphuric acid, however, is $1{\cdot}26 \times 10^{-2}$ ($pK_2 = 1{\cdot}90$), and when the pH is less than 1·90 (as it is in half the

cases dealt with in the paper) more than 50% of the total sulphate (c_{SO_4}) is in the singly charged state HSO_4^-, while even up to pH 2·63 (i.e. in all but two cases) it is not negligible; it *must*, therefore, be taken into account on its own and excluded from calculations concerned with the doubly charged SO_4^{2-} ion. Similarly, the total concentration of acid (c_H) is not a true measure of the free H^+ present, but includes the partly undissociated acid.

To show how important this effect is, the external concentrations of the ionic species present in each case have been calculated from Olofsson's data assuming pH = $-\log[H^+]$ and using the above value for K_2 in calculating $[HSO_4^-]_e$ and $[SO_4^{2-}]_e$ from the equations—

$$[HSO_4^-]_e = \frac{[H]}{[H] + K_2} c_{SO_4}$$

$$[SO_4^{2-}]_e = \frac{K_2}{[H] + K_2} c_{SO_4} \qquad \text{(i)}$$

The values for the external hydrogen and chloride ion concentrations were also calculated as follows—

$$[H^+]_e = c_H - [H_{SO_4^-}]_e$$

$$[Cl^-]_e = c_H - 2c_{SO_4} \qquad \text{(ii)}$$

and the results are shown in Table I.

Olofsson assumes that it is sufficiently accurate to take the total concentration of sulphate in the solution as equal to the concentration of SO_4^{2-} ions, but it is obvious from Table I that gross errors are involved, for—

$$c_{SO_4} = [HSO_4^-]_e + [SO_4^{2-}]_e$$

(Compare column 4 with the sum of columns 3 and 4 in Table I.)

With all these errors, it is not surprising that there are large divergences between the expected value of zero and Olofsson's calculations of—

$$-\log K = 2 \log \frac{[Cl]_I}{[Cl]_e} + \log \frac{[SO_4]_e}{[SO_4]_I} \qquad \text{(iii)}$$

Some of the deviations are, in fact, so large that they are obviously absurd, several being > 2, i.e. $K > 100$ when it should be 1; if the Donnan theory were really as bad as this, it would never have received consideration in the first place.

THE STATISTICAL TESTS

Olofsson then proceeds to use these inaccurate data to calculate the standard deviation of his $-\log K$ values to test statistically how significant is the difference between his mean value and that predicted by the Donnan theory. The fact that the fourteen differences in Olofsson's Table II [1] (columns (*c*) and (*d*), *loc. cit.*, p. 509) are all positive should make it immediately obvious that they are significant, quite apart from the *t*-test. But the deductions drawn by Olofsson from the significance of the *t*-values are so unexpected that it is necessary to discuss at some length the correct interpretation to be given to such results. To make the matter quite clear and incapable of misinterpretation, consider the following purely imaginary extreme case. Suppose two theories A and B

TABLE I

Donnan Calculations using Corrected Data

pH	External Ionic Concentrations (millimoles/litre) $[H^+]_e$	$[HSO_4^-]_e$	$[SO_4^{2-}]_e$	$[Cl^-]_e$	Combined Chloride (mmole/g.)	$\log \frac{\lambda_X}{\lambda_S}$ This paper *	Olofsson †
1·45	44·4	2·2	0·8	40·6	0·410	0·15	0·79
1·49	39·7	5·5	2·1	30·0	0·225	0·14	0·59
1·52	36·6	7·8	3·2	22·6	0·162	0·20	0·60
1·59	32·4	10·9	5·3	10·9	0·045	0·02	1·10
1·74	21·7	0·8	0·6	19·7	0·346	0·32	0·26
1·84	19·5	2·0	1·8	13·9	0·087	−0·03	0·06
1·90	17·1	3·4 5	3·4 5	6·8	0·114	0·60	0·10
2·09	8·7	0·1	0·2	8·2	0·243	0·33	0·49
2·27	7·6	0·2	0·5	6·4	0·133	0·27	0·39
2·32	6·7	0·4	1·1	4·1	0·057	0·23	1·12
2·37	4·5	0·08	0·22	4·0	0·195	0·66	0·57
2·63	3·6	0·08	0·42	2·7	0·041	0·13	0·71
2·98	2·6	0·008	0·092	2·4	0·063	0·16	0·64
3·29	1·4	0·004	0·096	1·2	0·031	0·18	1·42
					Mean	0·24	0·63

	Olofsson's Value of $-\log K$	Corrected Value $2 \log \frac{\lambda_X}{\lambda_S}$	Expected Value on Donnan Theory
	1·26	0·48	0·0
Standard deviation	0·77	0·37	
Departure from theory ...	1·26	0·48	
t-Value	6·1	4·6	

* Calculated from equations (viii) and (ix)

† Data obtained by halving the values given in column (*c*) of Table II (p. 509) of Olofsson's paper [1]

predict that a ratio of experimental determinations should be constant and have the value 0·0. Now suppose that the experimental data when applied according to A give ratios of −1, 0, 1, 2, 3, whose mean value is 1·0 and standard deviation 1·4; while theory B gives ratios of 0·01, 0·02, 0·01, 0·02, 0·01, whose mean is 0·014 and standard deviation 0·005. The statistics in case A lead to a t-value of 1·4 (only significant above the 20% level) and in case B to a t-value of 4·6 (highly significant at the 1% level). Is theory A, therefore, superior to B? Of course not! It is immediately apparent that A is a poor theory because (*a*) it does not give constant values, (*b*) there is a definite trend, and (*c*) the difference between the mean and the predicted values is far too large to be acceptable. On the other hand, theory B is eminently satisfactory since (*a*) the mean value differs from the expected value only by 0·014, (*b*) the values show no trend, and (*c*) they do not vary much. The high significance of the negligible difference of 0·014 merely implies that it is unlikely to be due to random effects. The statistics do not imply that this is a fault of theory B: it might equally be the result of a constant error in the apparatus, a mistake in arithmetic, or too drastic a simplification of the theory. It is also necessary to point out that the low t-value for A does not imply that its difference is not significant . . . it indicates only that its significance is *not proven*; in this case the high variability of the results masks the large departure from expectation. It can now be seen that the criterion for a good theory is not a small t-value but that (*a*) the difference between the expected and calculated values should be small, (*b*) the latter should be constant (small standard deviation), and (*c*) there should be no trend. In the light of these criteria it is now possible to examine the applicability of Olofsson's data to the Donnan and Gilbert–Rideal theories.

THE DONNAN THEORY

Part of the error in determining chloride concentration in Olofsson's paper[1] can, perhaps, be eliminated by estimating c_{Cl} indirectly from the other determinations. The corrected external concentrations are given in Table I, but, except for chloride, there is no exact way of determining the separate internal ionic concentrations, i.e. the fractions of the total combined sulphate present as SO_4^{2-} and HSO_4^-, since this requires a knowledge of the internal pH. However, the Donnan theory can be tested in the following way.

Let— $$\lambda_H = \frac{H}{h} \qquad \lambda_X = \frac{x}{X} \qquad \lambda_U = \frac{u}{U} \qquad \lambda_S = \sqrt{\frac{s}{S}} \tag{iv}$$

where H, h are $[H^+]$, X, x are $[Cl^-]$, U, u are $[HSO_4^-]$, and S, s are $[SO_4^{2-}]$, external and internal concentrations respectively. The Donnan theory requires that λ_H, λ_X, λ_U, and λ_S shall all be equal to $\lambda = e^{VF/RT}$, where V is the potential of the fibre phase.

For electrical neutrality of the external solution, it can be shown that the total concentrations of cations and anions in the fibre phase must be equal—

$$A_H - vu = A_X + v(u+2s) \tag{v}$$

where A_H is the amount of acid combined (including HSO_4^-), A_X is the amount of chloride combined, and v is the volume of the fibre phase. From equations (iv) and (v)—

$$\lambda_S^2 = \frac{A_H - A_X}{2vS} - \lambda_U \frac{U}{S} \tag{vi}$$

and this does not give a unique solution for either of the λs. But if it is assumed that λ_U is the same as λ_X (they both refer to singly charged anions) it is possible to test the theory by discovering how closely the value of λ_S, which can then be calculated from (vi), agrees with the value of λ_X estimated from the data directly.

Since $$A_X = vx \tag{vii}$$

then $$\lambda_X = \frac{A_X}{vX} \tag{viii}$$

whence $$\lambda_S = \sqrt{\frac{A_H - A_X\left(1+2\frac{U}{X}\right)}{2vS}} \tag{ix}$$

Using these equations and the corrected data, values of $\log(\lambda_X/\lambda_S)$ have been calculated and are given in the seventh column of Table I. According to the Donnan theory $\lambda_X = \lambda_S$ and the value of $\log(\lambda_X/\lambda_S)$, therefore, should be zero. This is not exactly obeyed, but the results are more reasonable than those of Olofsson, which are given in the last column, and they may be regarded as being not entirely inconsistent with the validity of the theory when due account is taken (*a*) of the inaccuracy of the experimental data and (*b*) of the considerations mentioned in the next paragraph. Such correction as has been possible reduces the difference between the expected and mean values of $-\log K$ from 1·26 to 0·48 and the standard deviation from 0·77 to 0·37; i.e. K is now much closer to 1·0 and is much less variable than would appear from Olofsson's analysis. The t-value for the corrected data is still large (4·6 instead of 6·1), but the significance may be due to residual, uncorrected errors in the experimental results or to the following consideration.

With such uncertain data it is useless to strive after precision by undertaking corrections for activity coefficients, although the above discrepancy of 0·48 may be due, in part, to this factor. Its contribution cannot be directly tested, as Olofsson attempts to do, because the published activity coefficients for sulphuric acid do not apply to sulphate ions since the data are uncorrected for the existence of considerable concentrations of the ion pair $NaSO_4^-$ (see Davies *et al.*[4]). Similarly, the data in a previous paper by Olofsson[5] cannot be correctly analysed without considering this anionic form of sodium—a form which must have given rise to the otherwise unaccountable apparent Na^+ combination.

THE GILBERT–RIDEAL THEORY

An important difference between the Donnan and Gilbert–Rideal theories is that, whereas the validity of the Donnan theory may be examined by testing whether the theoretical value of zero for $-\log K$ is obtained, no such simple and direct test of the Gilbert–Rideal theory is possible, because there is no theoretically expected value *a priori*. Olofsson assumes that a test of validity is possible by using data for the combination of keratin with sulphuric and hydrochloric acids separately to derive an estimate of the value to be expected for the mixed acids, whereas such a procedure merely indicates whether the several sets of data are consistent with one another. Since the titration curves of keratin with the separate acids are only 0·8 pH unit apart, the Gilbert–Rideal equation ought to give values for $-\log K$, in the case of the mixed acids, which should not differ from the expected values by more than this. The large standard deviations (0·8–1·0) of $-\log K$ on the Gilbert–Rideal theory, given in Olofsson's Table II[1], columns (*a*) and (*b*), are thus manifestly absurd and emphasise the inaccuracy of the uncorrected data.

The value of 1·24 for $-\log K$ (which is given in the same table as "expected") is also incorrect, as can be shown from the Gilbert–Rideal equations and the pH values at the midpoints of the hydrochloric acid–sulphuric acid–keratin titration curves as follows. The Gilbert–Rideal equation for the combination of pure hydrochloric acid is—

$$-\frac{\Delta\mu_{HCl}}{2{\cdot}3\,RT} = -\frac{\Delta\mu_H + \Delta\mu_{Cl}}{2{\cdot}3\,RT} = 2\text{pH} + \log\left(\frac{\theta}{1-\theta}\right)^2 \quad \text{(x)}$$

where $\Delta\mu$ is the affinity and θ is the amount of acid combined with the fibre, expressed as a fraction of the maximum acid-combining capacity. Writing $\text{p}K_X$ for the pH when $\theta = 0{\cdot}5$—

$$-\frac{\Delta\mu_H + \Delta\mu_{Cl}}{2{\cdot}3\,RT} = 2\text{p}K_X \quad \text{(xi)}$$

The corresponding equation for pure sulphuric acid is—

$$-\frac{\Delta\mu_{H_2SO_4}}{2{\cdot}3\,RT} = -\frac{2\,\Delta\mu_H + \Delta\mu_{SO_4}}{2{\cdot}3\,RT}$$

$$= 3\text{pH} + \log\left(\frac{\theta}{1-\theta}\right)^2\left(\frac{2\theta}{2-\theta}\right) \quad \text{(xii)}$$

and if $\text{pH} = \text{p}K_S$ when $\theta = 0{\cdot}5$—

$$-\frac{2\,\Delta\mu_H + \Delta\mu_{SO_4}}{2{\cdot}3\,RT} = 3\text{p}K_S - \log\frac{3}{2} \quad \text{(xiii)}$$

Olofsson has shown that, on the Gilbert–Rideal theory—

$$-\log K_{\text{expected}} = \frac{2\,\Delta\mu_{Cl} - \Delta\mu_{SO_4}}{2{\cdot}3\,RT} \quad \text{(xiv)}$$

and from the above equations it follows that—

$$-\log K_{\text{expected}} = 4\text{p}K_X - 3\text{p}K_S + \log\frac{3}{2} \quad \text{(xv)}$$

It is legitimate to take the pK values given by Steinhardt *et al.*[6], since their data were used by Olofsson: viz. $\text{p}K_X = 2{\cdot}32$ and $\text{p}K_S = 3{\cdot}08$ at 0°C., and $\text{p}K_X = 2{\cdot}17$ and $\text{p}K_S = 2{\cdot}97$ at 50°C. Interpolating for 22°C. (the temperature at which, presumably, Olofsson's data were obtained), $-\log K(\text{expected}) = 0{\cdot}061$, but the mean value calculated by Olofsson from his data is as large as 1·01, individual values being as high as 2·08, 2·11, and 2·49! The Gilbert–Rideal theory, however, is not really as unreliable as these results seem to suggest, since most of the divergence is probably due to the inaccuracy of the data.

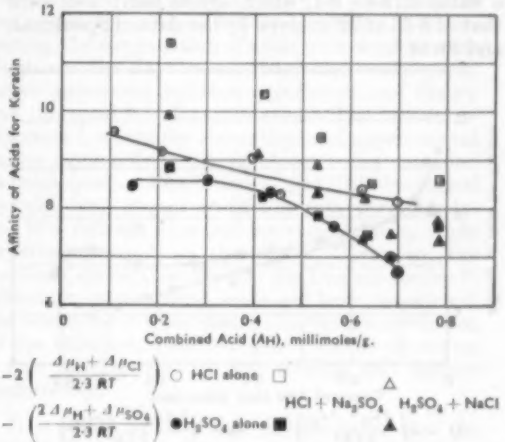

FIG. 1—Affinities of Keratin for Hydrochloric and Sulphuric Acids from Olofsson's Data calculated on the Gilbert–Rideal Theory

A much sounder estimate of $-\log K(\text{expected})$ may be obtained by calculating values of—

$$-\frac{2(\Delta\mu_H + \Delta\mu_{Cl})}{2{\cdot}3\,RT} \text{ and } -\frac{2\,\Delta\mu_H + \Delta\mu_{SO_4}}{2{\cdot}3\,RT}$$

from Olofsson's data at each pH value by means of equations (x) and (xii); the results are plotted in Fig. 1 against the amount of acid combined (A_H). The values are not constant (as they should be if the Gilbert–Rideal theory were strictly applicable), a definite trend being apparent, which also occurs with the data of other experimenters (see Fig. 2). Because of this trend, Olofsson appears to be in error in estimating $-\log K(\text{expected})$ from the mean of his values, since the number thus obtained is not a characteristic of the reaction, but is determined mainly by the choice of pH values at which the experiments were carried out. He should, instead, interpolate to find the point at which $A_H = 0{\cdot}43$ millimole/gram, i.e. where $\theta = 0{\cdot}5$ if A_{max} is taken as 0·86. It is this erroneous procedure which accounts for the difference between the above calculated value for $-\log K(\text{expected})$ (0·06) and that given by Olofsson (1·24). The correct value cannot be as large as 1·24, but it is not as small as 0·06, because the interpolated value of—

$$-\frac{2\,\Delta\mu_H + \Delta\mu_{SO_4}}{2{\cdot}3\,RT}$$

which I have calculated from the 1942 data for sulphuric acid at 0°C. (see Fig. 2) is not 9·06 (as it should be if $\text{p}K_S = 3{\cdot}08$ as stated by Steinhardt *et al.*[6]) but $8{\cdot}93 \pm 0{\cdot}02$. Olofsson states that Steinhardt's data yield a value of 7·5, but it is very difficult to understand how such a value could be obtained, since even the mean value is as high

as 9·16! He does not, however, use 7·5 but takes the mean value of 7·8 obtained from his own data for acids in presence of salts[5] and for sulphuric acid alone[1]. From Fig. 1, however, it can be seen that his results for mixtures when salts are present are so erratic that the true value, although greater than 8·2, is not determined with much precision; but the data of his later paper are consistent with a value of $8{\cdot}4 \pm 0{\cdot}1$, which agrees fairly well with that of 8·55 at 22°C. given by the data of Speakman and Stott[5].

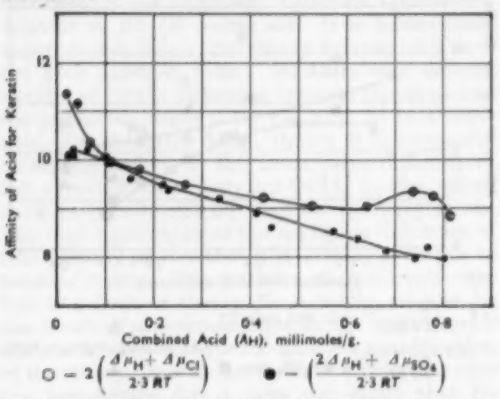

FIG. 2—Affinities of Keratin for Hydrochloric and Sulphuric Acids in Absence of Salts at 0°C. from Data of Steinhardt *et al.*[9] calculated on the Gilbert–Rideal Theory

Using published data for the combination of hydrochloric acid with wool keratin, similar calculations have been made of—

$$-\frac{\Delta\mu_H + \Delta\mu_{Cl}}{2{\cdot}3\,RT}$$

and interpolation gives 4·51[7] and 4·60[6] at 0°C., 4·40 at 22°C.[6], 4·25 at 25°C.[7], and 4·30 at 50°C.[6]; while $4{\cdot}16 \pm 0{\cdot}05$ is the best value obtainable from Olofsson's data[1] for hydrochloric acid in absence of salts at some unspecified temperature. The value when potassium chloride is present[7] varies with salt concentration, as shown in Fig. 3. It is very uncertain, therefore, what is the true value of $-\log K$(expected) with which to test Olofsson's data, but the values I have obtained from his experimental results lead to the estimate that—

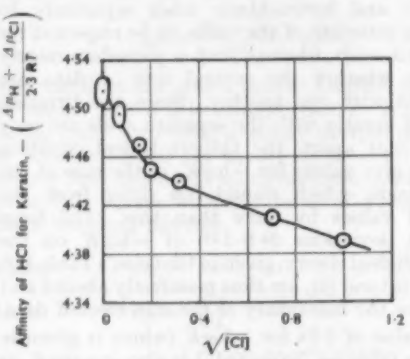

FIG. 3—Affinity of Keratin for Hydrochloric Acid in Presence of Potassium Chloride at 0°C. from Data of Steinhardt *et al.*[6] calculated on the Gilbert–Rideal Theory

$$-\log K_{\text{expected}} = 2(4{\cdot}34 \pm 0{\cdot}05) - 8{\cdot}32 \pm 0{\cdot}1 = 0{\cdot}36 \pm 0{\cdot}2$$

When this is compared with $-\log K$ calculated from the acid combined when both acids are present, it is mainly the self-consistency of the experimental data and hardly the Gilbert–Rideal theory which is being tested. In all the above calculations, HSO_4^- combination was assumed negligible, an assumption which supposes this anion to have no affinity for the protein at all.

TABLE II

Gilbert–Rideal Calculations using Corrected Data

pH	Amount of Ionic Combination (millimoles/kg.)				$-\log K$ calculated according to—		
	H^+	HSO_4^-	SO_4^{--}	Cl^-	(A)	(B)	Olofsson
1·45	609	117	41	410	0·90	2·27	2·49
1·49	544	179	70	225	0·73	0·65	0·95
1·52	520	196	82	162	0·77	0·68	0·81
1·59	469	214	105	45	0·34	0·24	1·12
1·74	566	92	64	346	0·99	0·89	0·79
1·84	527	128	111	177	0·66	0·76	0·52
1·90	541	143	143	114	0·33	1·17	2·08
2·09	452	51	79	243	0·74	0·62	0·26
2·27	489	63	147	133	0·60	0·45	−0·23
2·32	500	71	186	57	0·50	0·32	−0·11
2·37	338	21	61	195	1·22	1·17	1·18
2·63	373	28	152	41	0·12	0·00	1·17
2·98	255	8	92	63	0·06	0·00	1·05
3·29	121	2	44	31	0·29	0·27	2·11
Mean					0·59	0·68	1·01
Expected value					—	0·36	1·24
Standard deviation ...					0·45	0·57	0·80
t-Value					1·84	2·03	1·07
Departure from theory ...					—	+0·32	−0·23

Form what has already been said about the importance of this ion, it is obviously unjustifiable to ignore its concentration in solution, but there is no means of knowing what fraction of the total combined sulphate (A_{SO_4}) is in the doubly charged state, and what is in the partly undissociated form. Unfortunately, of the assumptions (A) that both forms are adsorbed in proportion to their concentration in solution, (B) that HSO_4^- ions have the same affinity for keratin as Cl^- ions, or (C) that HSO_4^- can be neglected, none yields a constant value for the affinity of SO_4^{2-} even at pH values at which practically all the sulphate in solution is present in that form. By ignoring the presence of HSO_4^- the variation in the apparent affinity of the sulphate ion is decreased and, at the same time, it is brought more nearly into coincidence with that of Cl^-, an ion for which partial association with H^+ can justifiably be neglected. But, however much one strives to interpret satisfactorily the data for mixed acids on the Gilbert–Rideal theory, one fails, because the theory does not hold adequately for the acids separately, so that there is no unique value to be expected for $-\log K$ at all points.

Nevertheless, in order to attempt to compare the applicability of the Gilbert–Rideal theory with the Donnan theory the following two extreme assumptions were made— (A) the sulphate adsorbed has the same ratio of HSO_4^- to SO_4^{2-} as the sulphate in solution, or (C) all the sulphate is present as SO_4^{2-} only. Values of $-\log K$ calculated from Olofsson's data using each of the above assumptions are given in Table II. Columns 6 and 7 were obtained with the corrected data and column 8 is taken from Olofsson's Table II, column (*a*), which corresponds to assumption (C).

From these values it can be seen that, when corrected data are used, the random variation is smaller (standard deviation 0·80 reduced to 0·57), while assumption (A) reduces it still further. The departure from theory is difficult to estimate, since $-\log K$(expected) has a variable value, as shown by Fig. 1–3.

The original Gilbert–Rideal theory assumed each multivalent anion to be adsorbed only at one positive site; Olofsson, however, has attempted to modify the equations for sulphuric acid adsorption to describe the case when each SO_4^{2-} is bound to two sites by writing $\theta_H = \theta_{SO_4}$ instead of $\theta_H = 2\theta_{SO_4}$. This is not sufficient, however, since the configuration of the positive sites and their distance apart also are involved, so that the true equations are more complicated. Olofsson's assumption would hold only if all positive sites occurred in pairs fairly close together. This would then require a more complicated equation for the adsorption of univalent anions. For these reasons it is, perhaps, better to ignore this possibility completely.

CONCLUSIONS

The Gilbert–Rideal theory does not satisfactorily apply to data for the combination of keratin with mixtures of hydrochloric and sulphuric acids because it predicts that $-\log K$ has a constant value, whereas, in fact with data for the separate acids, variable values are obtained even for the affinities ($\Delta\mu_H + \Delta\mu_{Cl}$) and ($2\Delta\mu_H + \Delta\mu_{SO_4}$) as well as for the difference ($2\Delta\mu_{Cl} - \Delta\mu_{SO_4}$), which corresponds to $2{\cdot}3\,\boldsymbol{RT}\log K$(expected).

The existence of the present problem is an indication of the great advance in the precision demanded by modern textile chemistry in interpreting the combination of acids with wool keratin. Gone are the days when rough-and-ready qualitative agreement between experiment and theory was acceptable. Interpretations like those of Harrison [9], where the theoretical and experimental curves agree only at one point, are today regarded as inadequate. The Donnan and Gilbert–Rideal theories both appear to fit the data very closely, and it is difficult to decide between them by crude experiments such as the above. Even so, the evidence, on balance, favours the Donnan theory [10]. Although only mineral acids are here considered, the results have repercussions on the interpretation of dye affinities, a subject which can be placed on a firm footing only by first settling this simpler controversy.

It is hoped to show in a further paper that the Gilbert–Rideal theory is only a special limiting case of the Donnan theory, and that the particular assumptions which characterise the Gilbert–Rideal treatment are not in accordance with other experimental data. In the meantime, however, false conclusions cannot be allowed to spread unchallenged, and the above criticism is, therefore, necessary to prevent misconceptions from being accepted because of the absence of specific rebuttal.

* * *

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(*Received 28th May 1953*)

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The Dyeing of Cellulose Acetate with Non-ionic Dyes

I—Absolute Heats of Association

T. G. MAJURY

The heats of dyeing of five "model" dyes on cellulose acetate have been measured. By combining these with the heats of solution and sublimation of the dyes, the absolute heats of association between dyes and substrate may be evaluated. This has been done for the two dyes for which data on heats of sublimation are available; values of the order of −20 kcal./mole are obtained. The bond energies appear to be chiefly ascribable to interaction between the permanent dipoles of the carbonyl groups in the substrate and permanent or induced dipoles in the dye molecules. There are indications in the two cases examined that, if intermolecular hydrogen bonds exist in the dye crystals, then hydrogen bonds may reasonably be postulated also between the dyes and the substrate.

INTRODUCTION

Investigations of cellulose acetate dyeing have so far dealt mainly with the mechanism of dye uptake, and little has been learnt about the forces of affinity operating between dye and substrate. A suggestion of hydrogen-bonding to the acetate carbonyl groups [1] is clearly inadequate, since many dyes contain no notable proton-donating groups, and another suggestion of hydrogen-bonding to the residual hydroxyl groups [2] is incorrect, since substances which dye secondary acetate also dye triacetate to the same extent, as will be shown here.

The large and important range of disperse dyes for cellulose acetate consists in general of azobenzene and anthraquinone derivatives. These share as common features a high degree of polarisability and, usually, a permanently polar character; in addition they often incorporate groups of hydrogen-bonding ability such as hydroxyl and primary and secondary amino groups. When these properties are considered in relation to the polarised carbonyl groups of the substrate there appear to be *a priori* three possible modes of interaction— (1) dipole–induced dipole, (2) dipole–dipole, and (3) the special form of dipole interaction known as hydrogen-bonding. To test these inferences and to find what contribution can be ascribed to each type of interaction, measurements of dyeing affinity have been made on cellulose secondary acetate and triacetate with a series of five model dyes. Grouping these dyes according to the possibilities of interaction suggested above, they were (1) *trans*-azobenzene, (2) *NN*-dimethyl-*p*-nitroaniline and *NN*-dimethyl-*p*-aminoazobenzene, and (3) *p*-nitroaniline and *p*-aminoazobenzene.

The results are interpreted in terms of the absolute heats of association between dye and substrate. These values are derived as follows—the heat of dyeing, which gives the heat of transfer of dye from solution to substrate, is combined with the heat of solution of the dye itself to give the heat of transfer of dye from dye crystal to substrate. If the heat of sublimation of the dye crystal is known, the absolute heat of association of the dye with the substrate can be evaluated. For example, in the case of *p*-nitroaniline on secondary acetate we have the following values—

Heat of solution	=	10·0 kcal./mole
Heat of dyeing	=	−7·1 kcal./mole
Heat of sublimation	=	24·7 kcal./mole

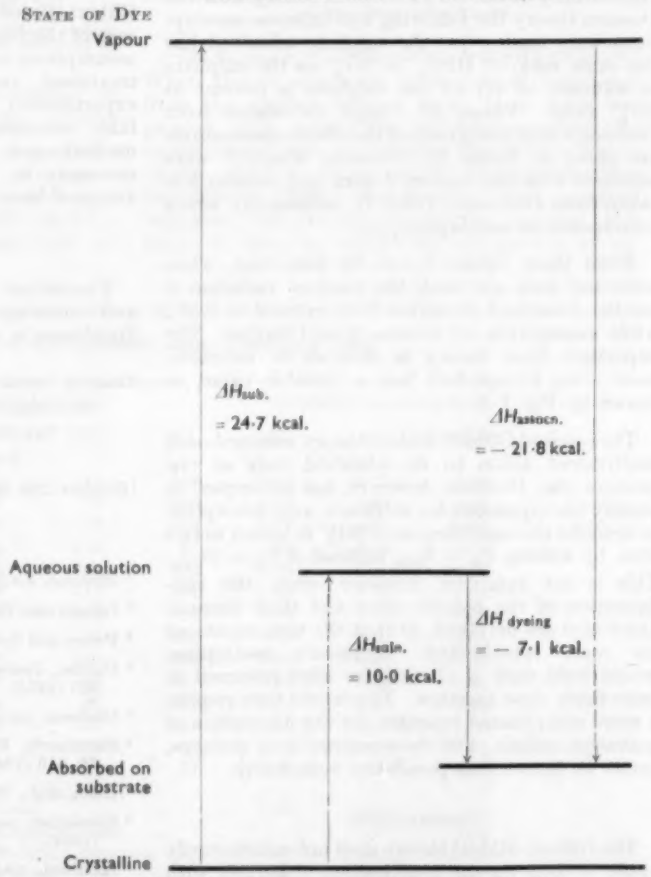

FIG. 1—Energy-level Diagram showing Derivation of Absolute Heat of Association of *p*-Nitroaniline on Secondary Cellulose Acetate

and the absolute heat of association is given by—

$$-24{\cdot}7+(10{\cdot}0-7{\cdot}1) = -21{\cdot}8 \text{ kcal./mole}$$

These changes in heat content are illustrated in an energy-level diagram in Fig. 1. Two assumptions are made in the derivation of the absolute heats of association— viz. that the dyes absorbed on the cellulose acetate are not solvated, and that the heat of wetting of the cellulose acetate is not altered as a result of the absorption of dye. The first assumption is reasonable in view of the hydrophobic nature of the dyes; the second is less certain, but its importance cannot yet be assessed in the absence of more comprehensive data on the moisture uptake of the substrate than those now available.

EXPERIMENTAL

Measurements were made of the amounts of dye taken up by cellulose secondary acetate and cellulose triacetate in equilibrium with aqueous dyebaths. The acetic acid values of the two acetates were 53·0% and 60·5% respectively. Both types of acetate were in the form of unplasticised film of 0·0045–0·005 cm. thickness. The dyes were B.D.H. Laboratory Reagents and were recrystallised from suitable solvents. The dyebaths were controlled within ±0·1°c. of the stated temperature and were stirred rapidly. The attainment of equilibrium absorption of dye was checked by repeated measurements over different times of dyeing.

To estimate the dye uptake, a weighed sample of film was dissolved in a solvent composed of methylene chloride and alcohol in the ratio 60 : 40 by volume and the solution was estimated photometrically on a Uvispek spectrophotometer. The amount of dye was expressed in terms of grams per litre of air-dry acetate using density values of 1·31 g./c.c. for the secondary acetate and 1·30 g./c.c. for the triacetate. It is assumed that the whole volume of the substrate is available for the uptake of these dyes, or in other words that the acetate phase constitutes a homogeneous solution of the dyes.

The solubilities in water of each dye were measured at the dyeing temperatures. Those of *p*-nitroaniline were measured by the evaporation and weighing of filtered solutions, and those of the less soluble compounds by extraction of filtered solutions with methylene chloride followed by addition of alcohol and photometric estimation on a Uvispek spectrophotometer.

The experiments were carried out at temperatures of 60° and 80°c. This rather narrow range was imposed by two conditions— viz. structural changes in the acetate at temperatures much above 80°c. and excessive slowness of absorption below 60°c. However, the uncertainty of absolute heat of association (approx. ± 2 kcal./mole) resulting from these restrictions does not affect the conclusions to be drawn.

RESULTS

The experimental results are presented in Table I.

DISCUSSION

The results for cellulose secondary acetate will be considered first.

The linearity of the dyeing isotherms was checked in the cases of *p*-nitroaniline and *p*-aminoazobenzene. This linearity, which has been reported previously for various amines and phenols on cellulose acetate [3] and cellulose nitrate [4] and more recently for a commercial dye on cellulose acetate [5] and various derivatives of anthraquinone on cellulose acetate [6] and Terylene [7], has the advantage of making the thermodynamical calculations much more straightforward than they are,

TABLE I

Summary of Experimental Results

Dye	Temp. (°c.)	Dyebath Concn. (g./litre)	Secondary Acetate Uptake (g./litre)	Secondary Acetate Partition Coefficient	Secondary Acetate Free Energy of Dyeing (kcal./mole)	Triacetate Uptake (g./litre)	Triacetate Partition Coefficient	Triacetate Free Energy of Dyeing (kcal./mole)
p-Nitroaniline	60	1·00	55·4	55·4	−2·68	—	—	—
		2·83*	160	56·5		150	53·0	−2·64
	80	0·20	7·0	35·0		—	—	—
		2·00	60·1	30·1		—	—	—
		5·00	151	30·2		—	—	—
		6·59*	197	29·9	−2·40	169	25·6	−2·29
NN-Dimethyl-*p*-nitroaniline	60	0·092*	17·0	185	−3·48	22·0	239	−3·65
	80	0·250*	23·5	94	−3·20	25·4	102	−3·26
Azobenzene	60	0·0293*	59·0	2,010	−5·06	—	—	—
	80	0·0760*	56·3	740	−4·66	63·4	833	−4·74
p-Aminoazobenzene	60	0·153*	161	1,050	−4·63	134	876	−4·51
	80	0·110	51·1	465		—	—	—
		0·370*	185	500	−4·35	174	470	−4·34
NN-Dimethyl-*p*-aminoazobenzene	60	0·0060*	23·5	3,920	−5·50	—	—	—
	80	0·0167*	24·9	1,490	−5·15	31·3	1,875	−5·31

* Saturated

for instance, in the case of cellulose. Here the values for the free energy (affinity) and the heat of dyeing have been calculated directly from the equations—

$$\ln K = -\frac{\Delta G}{RT}$$

$$\Delta H = \frac{RT_1T_2}{T_1 - T_2} \ln \frac{K_{T_1}}{K_{T_2}}$$

where K is the partition coefficient and ΔG and ΔH are the free energy and heat of dyeing. Similar calculations on the solubility data gave the heats of solution of the dyes in water.

Combining the heats of solution and of dyeing we obtain the heats of association of the dyes with cellulose acetate relative to their heats of association with neighbouring dye molecules in the dye crystal. If the crystal energy, i.e. the heat of sublimation of the dye crystal, is known, we can evaluate absolutely the heat of association of the dye on the substrate. Unfortunately, published values for the heats of sublimation can be found only for *p*-nitroaniline and azobenzene. The information thus available is summarised in Table II.

It can be seen that the dye–substrate association is similar in strength to the dye crystal association and is of the order of −20 kcal./mole. In some recent work with a commercial acetate dye the dye–substrate bond strength has been identified with the heat of dyeing and the typical value of 10·5 kcal. has been attributed to two hydrogen bonds [5]. However, it appears from these results that the actual binding force is probably much higher than this, and other more important forces must be considered. (It should be noted that, since azobenzene is molten at the upper limit of temperature, the values for its heat of solution and hence of its absolute heat of association are probably somewhat low.) The heats of association relative to the dye crystal are roughly constant within each group of dyes, viz. 3–4 kcal. for the nitroanilines and 0–1 kcal. for the azobenzenes, so that the absolute strengths of the dye–substrate bonds in each group stand in the same relation to one another as the strengths of the corresponding dye–dye bonds. Some idea of the latter relation may be deduced from the hydrogen-bonding and the polar properties of the dyes as expressed in terms of their molar refractions (electron polarisabilities, P_E) and dipole moments. These are given in Table III.

The polar properties of the two nitroanilines do not differ greatly, and any difference in their crystal energies might be expected to arise from the presence of intermolecular hydrogen-bonding possibilities in the crystalline primary amine. It has been suggested [10] that there may be a rather weak hydrogen bond here, say 3 kcal., so that the heat of sublimation of the methylated compound might be assigned a value of 22 kcal./mole. The absolute heat of association of this compound on cellulose acetate would then be 18 kcal. The value for *p*-nitroaniline exceeds this by 4 kcal., a difference which can reasonably be ascribed to hydrogen-bonding to the carbonyl oxygen atoms.

The value thus deduced for *NN*-dimethyl-*p*-nitroaniline is close to that found for azobenzene, which has approximately the same polarisability but zero net dipole moment in contrast to the large moment of the nitroaniline. Two possibilities may be suggested. In azobenzene the absence of dipole moment is known to be due not to the absence of polarity but to the cancelling of two equal and opposite moments; at short distances of approach to another permanent dipole this quadrupolar character is likely to become important in establishing interaction. Secondly, it may be that polarisability rather than permanent polarity is the predominating factor in determining bond strengths, i.e. that the bonds are substantially of the dipole–induced dipole type. That polarisability appears to exert some influence was shown by treating samples of cellulose acetate with aqueous and alcoholic carotene for several weeks at 80°C. Both samples took up the carotene uniformly. Since this substance is highly conjugated and hence highly polarisable, but unlikely to contain any large permanent displacements of charge, this evidence may be taken as qualitative confirmation of the importance of the polarisability of a dye in establishing interaction with cellulose acetate.

NN-Dimethylaminoazobenzene, which has permanent polarity and also higher polarisability than azobenzene, may be expected to have a somewhat larger heat of sublimation and hence a larger heat of association with cellulose acetate. The heats of sublimation and of association of aminoazobenzene will probably be larger still owing to the possibility of hydrogen-bonding. But quantitative knowledge of the interaction of these dyes with cellulose acetate must await determinations of their heats of sublimation.

The results for cellulose triacetate do not differ significantly from those for secondary acetate.

TABLE II

Measured Heats of Solution, Dyeing, and Sublimation and Deduced Heats of Association

(Secondary acetate; kcal. per mole of dye)

Dye	Heat of Soln.	Heat of Dyeing	Heat of Sublimation	Heat of Association relative to Dye Crystal	Absolute Heat of Association
p-Nitroaniline	10·0	−7·1	24·7 [9]	−2·9	−21·8
NN-Dimethyl-*p*-nitroaniline ...	11·8	−8·0	—	−3·8	—
Azobenzene	11·2	−11·8	17·7 [9]	+0·6	−18·3
p-Aminoazobenzene	10·4	−9·2	—	−1·2	—
NN-Dimethyl-*p*-aminoazobenzene	12·1	−11·3	—	−0·8	—

Since, then, the two acetates have the same affinity for a given dye, it may be concluded that the origin of this affinity is in the acetyl rather than in the hydroxyl group. The proportion of acetyl groups present is evidently not a limiting factor, within this range, in determining dye uptake. This is perhaps not unexpected in view of the actual amounts of dye taken up. For example, even with the greatest uptake of the smallest dye molecule on secondary acetate (15% *p*-nitroaniline), the ratio of dye molecules to acetyl groups is only 1 : 9.

TABLE III

Electron Polarisabilities and Dipole Moments

Dye	P_E (c.c./mole)	μ (e.s.u. $\times 10^{18}$)
p-Nitroaniline	41 [11]	6·3 [11]
NN-Dimethyl-*p*-nitroaniline	56 [12]	6·9 [15]
Azobenzene	62 [13]	0 [16]
p-Aminoazobenzene ...	71 [14]	2·7 [14]
NN-Dimethyl-*p*-aminoazobenzene	79 [13,14]	3·2 [13,14]

* * *

We are indebted to Lansil Ltd. for gifts of cellulose secondary acetate and triacetate and to Bexford Ltd. for a gift of cellulose triacetate.

Much of the experimental work on which this paper is based was carried out by Mr. A. Hanrahan.

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The Dyeing of Cellulose Acetate with Non-ionic Dyes

II—Rates of Diffusion and their Relation to Dyeing Affinity

T. G. MAJURY

Measurements of the rates of dyeing of five "model" dyes on cellulose secondary acetate and triacetate have been used to evaluate the apparent diffusion coefficients of the dyes. The coefficients are shown to have a twofold activation energy: one part is identifiable with the free energy of dyeing, and the other is attributable to mechanical obstruction of the diffusing dye by the body of the substrate. This suggests that a dye molecule penetrating cellulose acetate undergoes alternate absorption by the acetate and solution by the water, and that diffusion takes place in the aqueous phase.

The two main characteristics of dyeing behaviour — equilibrium uptake and rate of dyeing — have been studied for the following series of model dyes on cellulose secondary acetate and triacetate—*p*-nitroaniline, *NN*-dimethyl-*p*-nitroaniline, azobenzene, *p*-aminoazobenzene, and *NN*-dimethyl-*p*-aminoazobenzene. The reasons for this choice and the results of the equilibrium measurements have been given in the preceding paper; the present paper is concerned with the results of the rate measurements.

EXPERIMENTAL

The materials and the methods of measurement were the same as those described in the earlier paper. Preliminary tests showed that the rates of dyeing were very dependent on the circulation of the dyebath; it was finally found best to place loose samples of film approx. 2 cm. square in dyebaths of standard size and shape and to stir at a standard speed of 1,200 r.p.m. by means of a small glass propeller in each bath.

Given adequate circulation of the dye liquor, the rate of dyeing is controlled by the rate of diffusion of the dye in the substrate, and this rate is most concisely expressed by the diffusion coefficient of the dye. If we assume that the diffusion coefficient is independent of concentration, it is simple to deduce its value by fitting the experimental dyeing curve to the ideal curve applied by McBain to absorption by an infinite plane slab [1]. In general this assumption is not justified, and the apparent diffusion coefficient measured by reference to McBain's equation cannot be interpreted quantitatively with great certainty. But it still gives a concise expression of the dyeing rate for specified conditions of concentration and will serve, for

example, in comparing the dyeing behaviour of two samples of acetate differing from one another in structure.

RESULTS

These apparent diffusion coefficients have been evaluated for the abovementioned dyes on cellulose secondary acetate (53% acetic acid) and cellulose triacetate (60·5% acetic acid). The results are summarised in Table I.

DISCUSSION

A test of concentration dependence of the diffusion coefficient was made only for *p*-nitroaniline, since the low solubilities of the other compounds made it impossible to maintain constant concentration throughout dyeing except in saturated solutions, or solutions of unmanageably large volume. The results show no evidence of concentration dependence; those obtained at 60°C. are more reliable than those at 80°C. owing to the great speed of absorption at the higher temperature.

Comparing the dyes, the results on each type of acetate place the diffusion coefficients in the same relationship to one another. This relationship is closely connected with the free energies of dyeing, as can be seen from Fig. 1, in which $\ln D$ is plotted against $-\Delta G/RT$ (see preceding paper for values of ΔG), and leads to a very interesting result.

Since diffusion is an activation-controlled process, the diffusion coefficient can be represented as—

$$D = C_1 e^{-\Delta H_{dif}/RT} \times e^{\Delta S_{dif}/R} \quad \text{(i)}$$

$$= C_1 e^{-\Delta G_{dif}/RT} \quad \text{(ii)}$$

where ΔH_{dif}, ΔS_{dif}, and ΔG_{dif} are respectively the heat, entropy, and free energy of activation for diffusion and C_1 can be regarded as substantially constant[3]. Taking natural logarithms, we have—

$$\ln D = C_2 - \frac{\Delta G_{dif}}{RT} \quad \text{(iii)}$$

where $C_2 = \ln C_1$.

In Fig. 1 we have a set of experimental relations between $\ln D$ and $-\Delta G/RT$, where ΔG is the free energy of dyeing, for two types of acetate at two temperatures. These can be represented reasonably well as four straight lines each of slope −1, so we have also the experimental relation—

$$\ln D = C_3 - \frac{-\Delta G}{RT} \quad \text{(iv)}$$

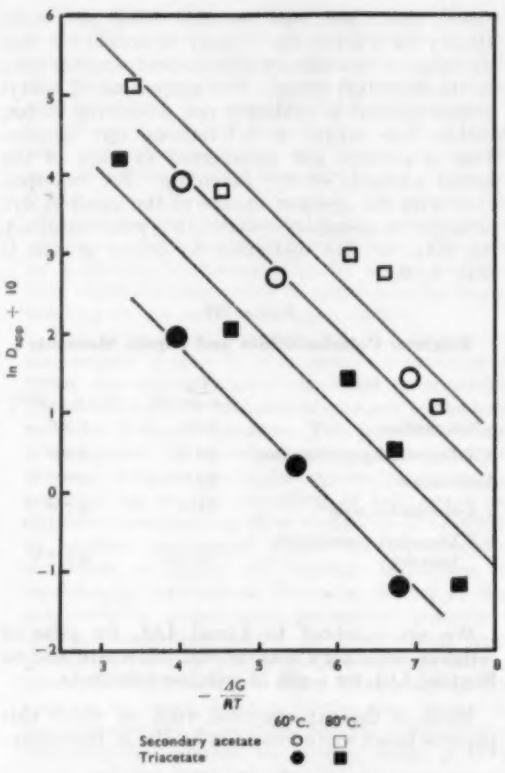

FIG. 1—Plots of $\ln D_{app}$ against $-\Delta G/RT$

where C_3 is a constant for a given substrate at a fixed temperature.

Comparing these two equations for $\ln D$, we find—

$$\Delta G_{dif} = -\Delta G + (C_3 - C_2)\,RT \quad \text{(v)}$$

i.e. the free energy of activation for diffusion is composed of two parts, one of which is equal and opposite to the free energy of absorption of the dye. This is consistent with the view that a prerequisite for diffusion is the release of the dye-molecule from the substrate to the solution which permeates the substrate. To effect this release the absorbed dye molecule must acquire thermal energy corresponding to the heat of dyeing ΔH; on release its

TABLE I

Apparent Diffusion Coefficients of Various Model Dyes in Cellulose Secondary Acetate and Triacetate

Dyebath	D_{app} (sq. cm./sec. × 10^{10}) Secondary Acetate			Triacetate		
	60°C.	80°C.	$\frac{D_{80°}}{D_{60°}}$	60°C.	80°C.	$\frac{D_{80°}}{D_{60°}}$
p-Nitroaniline 0·1%	46	—	—	—	—	—
0·2%	—	130	3	—	—	—
*	52	200	4	7·2	67	10
NN-Dimethyl-*p*-nitroaniline* ...	15	45	3	1·4	8·0	6
Azobenzene*	—	16	—	—	1·7	—
p-Aminoazobenzene*	4·3	20	5	0·3	4·2	14
NN-Dimethyl-*p*-aminoazobenzene*	—	2·9	—	—	0·3	—

*Saturated solutions—actual concentrations given in preceding paper

TABLE II

Comparison of Activation Energies of Diffusion in Secondary Acetate and Triacetate

(kcal. per mole)

Dye	Secondary Acetate			Triacetate		
	ΔH_{diff}	$-\Delta H$	$\Delta H'$	ΔH_{diff}	$-\Delta H$ (approx.)	$\Delta H'$
p-Nitroaniline	15	7	8	26	7	19
NN-Dimethyl-*p*-nitroaniline ...	13	8	5	20	8	12
Aminoazobenzene	18	9	9	31	9	22

entropy increases by ΔS, the entropy of dyeing, and the net increase in free energy is equal to $-\Delta G$.

This leads to a consideration of the other component of the total free energy of activation, $\boldsymbol{RT}(C_2-C_3)$, which will now be denoted by $\Delta G'$. Since ΔG_{diff} cannot be measured, $\Delta G'$ is likewise unattainable. But these free energy terms can be divided into their heat and entropy components, and assuming as a reasonable approximation that the latter are temperature-independent they may be equated separately, thus—

$$\Delta G_{diff} = -\Delta G + \Delta G' \qquad \text{(vi)}$$

whence—

$$\Delta H_{diff} = -\Delta H + \Delta H' \qquad \text{(vii)}$$

$$\Delta S_{diff} = -\Delta S + \Delta S' \qquad \text{(viii)}$$

The total heats of activation ΔH_{diff} can be derived from the temperature coefficients of diffusion and the heats of dyeing ΔH are already known from equilibrium dyeing measurements (see preceding paper for values), so that $\Delta H'$, the partial heat of activation for diffusion corresponding to $\Delta G'$, can be obtained as the difference between the total heat of activation for diffusion and the heat of dyeing. The values obtained for $\Delta H'$ are given in Table II. It will be seen that they are partly dependent on the dye in question (it is this dependence which gives rise to the systematic deviations shown in Fig. 1), but that the chief difference lies between the values for the two types of acetate, those for triacetate being 7–13 kcal. higher than those for secondary acetate. These facts suggest that $\Delta H'$ may be interpreted as due to the obstruction offered to diffusing dissolved dye by the body of the substrate.

The reason for the large difference in $\Delta H'$ between secondary acetate and triacetate is not yet known, but is possibly connected with the reduced swelling in water of the triacetate. Experiments on structural modification of the acetates are in hand which may lead to an understanding of this point.

Finally it may be pointed out that equation (iv) verifies an expression given by Wilson for the apparent diffusion coefficient in the case of simultaneous diffusion and absorption[3]. In this derivation the dye was regarded as diffusing in aqueous solution permeating capillaries in the substrate, with absorption of dye by the capillary walls taking place concurrently. Considering the partition coefficient K to be independent of concentration, and absorption to be rapid compared with diffusion, it was shown that the apparent diffusion coefficient is related to the "true" coefficient for diffusion in the capillaries D_0 by the equation—

$$D_{app} = \frac{D_0}{K+1} \qquad \text{(ix)}$$

Taking natural logarithms, for sufficiently large values of K we have—

$$\ln D_{app} = \ln D_0 - \ln K \qquad \text{(x)}$$

$$= \ln D_0 + \frac{\Delta G}{\boldsymbol{RT}} \qquad \text{(xi)}$$

since $K = e^{-\Delta G/\boldsymbol{RT}}$, where ΔG is the free energy of dyeing. This is the same as equation (iv) if we identify C_3 in the latter with $\ln D_0$. (Evidence for the partition coefficient being independent of concentration was given in the preceding paper.)

* * *

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The Editor does not hold himself responsible for opinions expressed by correspondents

The Dyeing of Cellulose Acetate from the Vapour Phase

The heat of association derived in Part I of my communication[1] should be numerically equal to the heat of dyeing from vaporised dye, i.e. to the heat which would be evolved if one mole of dye in the vapour state were transferred directly to the acetate. Clearly, a study of the cellulose acetate–dye-vapour–solid dye system might lead to a direct method of measuring the absolute bond-strength between dye and substrate, with the simplifying advantage that the presence of water is eliminated, and we are now setting out to study systems of this kind. Briefly, our experiments consist in enclosing samples of dye and of cellulose acetate film in separate limbs of an inverted **U**-tube, which is then evacuated to 10^{-4} mm. of mercury and sealed off. The limbs are immersed in adjoining thermostats, so that the acetate sample is at a temperature equal to or greater than that of the dye. The progress of sorption is followed by opening tubes after different time intervals and measuring the dye uptake by a standard method. Provision is being made to measure the vapour pressures and heats of sublimation of the dyes at the temperatures employed.

Preliminary work has shown that the "model" dyes previously employed in aqueous dyeing (*p*-nitroaniline, *NN*-dimethyl-*p*-nitroaniline, azobenzene, *p*-aminoazobenzene, and *NN*-dimethyl-*p*-aminoazobenzene) all dye satisfactorily by this method, so that eventually an interesting comparison of results should be possible. It is hoped to publish full details of the method and results in due course.

T. G. Majury

The British Rayon Research Association
Heald Green Laboratories
Wythenshawe
Manchester

29th June 1954

[1] Majury, T. G., J.S.D.C., **70**, 442 (Oct. 1954).

Variables in Padding Processes

It was refreshing and interesting to read R. W. Speke's paper in the June issue of the *Journal*[1]. No doubt that all readers congratulate him on the organisation of his comments and the review he was able to give in a comparatively short discourse.

It will have come as a shock to those of my era to read that pads are now considered an essential, since the more sprightly used them before 1914 and for systems of pigment-padding from about 1919.

It is a pity, I think, that Speke did not discuss the three-bowl pad more fully, as, of course, it is more important than the two-bowler. But, apart from that, it seems to be a strange kink in all technical brains only to consider pads as vertical machines, and it comes almost as a shock when technologists are reminded of the alternative horizontal pads.

I must raise issue with Speke about his tangentially placed bar or roller, and I would undoubtedly ask the engineer to remove it to avoid an almost certain "variable". I am in full agreement with him that every attention must be given to the hardness–softness of the nips, though I might want to argue the size of the rollers. Impression along with the required expression are most important where maximum penetration is wanted.

In my view, and I always practise it, intermediate drying is most valuable when pigment-padding, but I would exceed the courtesy of the correspondence column if I enlarged on the reasons. Similarly, I always recommended intermediate drying with Soledon (ICI) types when medium shades were demanded and, although dye migration would follow, it was possible to get such darker shades at reasonable cost with still satisfactory penetration.

Finally, may I endorse Speke's comments about thorough and proper preparation of pieces prior to padding? Dyes should not be repelled by waxy remains nor should they be used to dye sizes. I see no particular difficulty in a form of continuous preparation and do not regard that as a problem. But that is another story.

Herbert à Brassard

136 Grove Hall Court
Hall Road
London N.W.8

7th August 1954

[1] Speke, R. W., J.S.D.C., **70**, 221 (June 1954).

It is apparent that the author and Mr. H. à Brassard are in substantial agreement on the subject of "pads" and "padding". The difference of opinion on the merits of the tangentially placed guide bar provide an excellent illustration of the fact that specific local conditions and requirements can affect the significance of a given variable.

R. W. Speke

Dyehouse Department
Imperial Chemical Industries Ltd.
Hexagon House
Manchester 9

10th August 1954

Fibravyl, Rhovyl, and Thermovyl

In the interesting paper by Kramrisch and Bratt in the May issue of your *Journal*[1], it is stated that "vinyl polymer fibres such as Fibravyl, Rhovyl, and Thermovyl tend to shrink to an appreciable degree even well below the boil, and if possible the garment dyer is advised to avoid processing them".

According to this sentence, these three fibres shrink at temperatures well below the boiling point of water. Now, even though it is true that Rhovyl and

Fibravyl undergo appreciable shrinkage at temperatures below 100°C.—a shrinkage which, incidentally, finds application in the production of effects in fabrics—Thermovyl, a thermally stabilised fibre, may be brought to boiling point without appreciable shrinkage, provided, of course, that it has undergone during spinning no accidental stretching which might modify the properties of the fibre.

We should be very obliged if you would publish a correction on this point in an early issue of your *Journal*.

SERVICE DÉVELOPPEMENTS
SOCIÉTÉ "RHOVYL"
TRONVILLE-EN-BARROIS
(MEUSE)
FRANCE

22nd July 1954

[1] Kramrisch, B., and Bratt, A. E., J.S.D.C., **70**, 175 (May 1954).

Notes

Extraordinary General Meeting President-elect of the Society

At an Extraordinary General Meeting of the Society held at the Victoria Hotel, Bradford, on Wednesday, 8th September 1954, Mr. CLIFFORD PAINE, B.Sc., Chairman of the Dyestuffs Division of Imperial Chemical Industries Limited, was unanimously elected President-elect of the Society, in accordance with the recommendation of the Council.

The President (Mr. FRED SMITH, F.S.D.C.), in proposing Mr. Clifford Paine, referred to the bereavement the Society had suffered by the death of its former serving President, Mr. F. L. Goodall, which had sadly advanced the speaker's own elevation from President-elect to be President. The Council had deemed it desirable that the vacancy thus created of President-elect should be filled, and the Society was now greatly honoured to have for this position Mr. Clifford Paine, who was so well qualified to become in due course its President.

Mr. G. S. J. WHITE, M.A., F.T.I., F.S.D.C., Vice-chairman of the Council, seconding, suggested that the Society would be greatly advantaged by having Mr. Clifford Paine to assist the President in negotiations with the chemical societies in furthering arrangements for the Perkin Centenary Celebrations now being planned for 1956.

Meetings of Council and Committees September

Council—8th
Finance—8th
Fastness Tests Co-ordinating—9th
Diplomas Executive Subcommittee—20th
Publications—21st
Colour Index Editorial Panel—22nd
Northern Ireland Symposium—25th

Death

We regret to report the loss by death of Mr. T. A. Hume.

Society's Diplomas Scheme

ASSOCIATESHIP

The 1954 examinations for the Associateship will be held in Bradford and Galashiels on 11th, 12th, and 13th November 1954.

FELLOWSHIP

As was stated when the previous list of awards was published (J.S.D.C., **70**, 155 (April 1954)), recognition of overseas members has been receiving earnest consideration, as a result of which the following have been elected Fellows of the Society—

William Dunford Appel
Werner von Bergen
William Hamlin Cady
Wilfrid Curtis Castle
Louis Diserens
Nils Gralén
Felix Erhard Gund
Emil Adolf Krähenbühl
Charles August Muhr
Charles Norris Rabold
George Lewis Royer
Ernest Sack
Gustav Schwen
Werner Stauffacher
Emery Imre Valko
Krishnasami Venkataraman

A.S.D.C. Lectures in Nottingham

Classes covering the syllabus for Papers A and B of the Associateship examination have commenced at the Nottingham and District Technical College. They occupy two evenings per week.

Swedish Dyers' Conference of 1954

The annual conference of Svenska Färgeritekniska Riksförbundet was held this year at Gävle, on the east coast of Sweden, on August 20th–22nd. The undersigned two members of the Society of Dyers and Colourists were fortunate in being able to attend this function, and as part of their remit conveyed formally to the Swedish society the good wishes and greetings of its British counterpart, sentiments which were heartily reciprocated.

The S.F.R. was formed in 1924 and now has active branches at Gothenburg, Borås, Malmö, Norrköping, and Gävle. An official journal, *Färgeriteknik*, is published monthly. The President, Hr. Agaton Mars, is a founder member

who has given many valuable years of service to the dyeing and finishing industry.

The scope of the conference was typical of the progressive nature of the Swedish dyeing and finishing industry, an industry that is in the main organised vertically and characterised by the excellence of its equipment. The party, some one hundred strong (wives included), assembled on Thursday afternoon, many having travelled long distances to attend, and the proceedings started with a visit to a combined wool and viscose rayon factory, Gävle Angväfveri. On the Friday morning, while the men were visiting the extensive paper mill, Korsnäsverken, the ladies were taken on a tour of the local porcelain factory, Porslinsfabriken. After lunch, lectures were given on *New Developments in the Naphtol AS Series* and *The Dyeing of Synthetic Textile Fibres in France* by W. Gronen and M. P. Niederhauser respectively. These were followed by the annual general meeting of the society, and the lengthy day's programme was terminated with a formal dinner and dance. While many departed homewards early on the Sunday, various diversions were provided for those who could make it a long week-end.

Your correspondents will retain nothing but pleasant memories of the excellence of the Swedish hospitality and welcome extended on this particular occasion.

R. W. SPEKE
E. WATERS

Eleventh Olney Medal

The Olney Medal, the highest award of the AATCC, was presented to William D. Appel, chief of the Textile Section of the National Bureau of Standards in Washington, at the National Convention of the Association in Atlanta on 16th September 1954.

Japanese Dye Exports

Japanese exports of dyes in the first six months of 1954 were approx. 1100 metric tons, an increase of 10% on those for the same period in 1953. The following are the figures (in metric tons) issued by the Japanese Finance Ministry—

	1953 1st Half	1953 2nd Half	1954 1st Half
Basic... ...	10	41	34
Direct ...	113	196	97
Acid ...	15	31	39
Mordant ...	2	4	4
Sulphur ...	562	656	805
Indigo ...	324	*	*
Vat	10	16	12
Fat-soluble ...	*	1	—
Lake ...	13	42	23

* Less than 500 kg.

C O C

ERRATA

The patent numbers listed below should be corrected as shown—

J.S.D.C., 70 (1954) Month	Page	Patentee	Number of Patent As printed	Corrected
Jan.	31	Minnesota Mining & Manufacturing Co.	*USP* 2,262,883	*USP* 2,[illegible]5,883
March	125	Courtaulds	*BP* 701,801	*BP* 701,861
	135	General Aniline	*BP* 710,341	*BP* 701,341
	136	V. Golden	*BP* 2,629,919	*USP* 2,629,919
May	192	Butterworth & Furnival	*BP* 702,792	*BP* 704,792
	195	Colgate-Palmolive-Peet Co.	*USP* 704,391	*BP* 704,391
	203	Kodak	*BP* 703,526	*BP* 703,520
June	247	Standard Dyewood Co.	*BP* 704,408	*BP* 703,408
	252	DuP	*BP* 702,807	*BP* 702,867
	255	Koppers Co.	*BP* 707,203	*BP* 707,263
		American Viscose Corpn.	*USP* 2,638,743	*USP* 2,638,734
July	320	Ciba	*BP* 708,114	*BP* 708,144
Aug.	370	Plastanol	*BP* 710,441	*BP* 710,414
	374	Union Française Commerciale et Industrielle	*BP* 710,	*BP* 710,134

In *BP* 702,910 (J.S.D.C., **70**, 220 (May 1954)) the patentees are R. Kreutzer and G. Wissmuller trading as J. S. Staedtler.

OBITUARY NOTICE

Fred Wilkinson

The recent sudden death of Mr. Fred Wilkinson at the age of eighty years removes one of the staunchest supporters of the Society of Dyers and Colourists. His father, the late Mr. J. B. Wilkinson, was a founder member of the Society who always attached great value to its *Journal*, and it was on his motion, at the preliminary meeting held at the then only recently opened Bradford Technical College, at which the formation of the Society was decided upon, that the decision to print its transactions in a journal of its own was carried. Mr. J. B. Wilkinson could therefore be styled the father of our *Journal*, and his son Fred was realistically born and reared in the very atmosphere of the Society. His subsequent early zeal for its welfare, and his wholehearted support of its activities after his father's demise in 1920, are therefore very

readily to be understood. Seldom was he absent from the Annual Meeting and Dinner, and usually he was to be found at the Society's lectures and other functions.

Fred Wilkinson was born at Lockwood, Huddersfield, in 1873, but his long association with Bradford began when his father migrated to Dudley Hill in 1878, and, at the early age of 10, he actually helped his father, who had then commenced business on his own account at the Ivy Works, Dudley Hill, in 1882, subsequently to be transferred to the present site in Holme Lane in 1888. At the age of 15, Fred visited France for six months to study the language, and on his return, he worked full time in his father's business and also attended evening classes in Chemistry, French, and German at the Bradford Technical College. On the death of his father in 1920, Fred continued the business in partnership with his elder brother, George, until 1932, when he became sole owner. It was made into a limited company in 1948, when Fred became Chairman and Managing Director of J. B. Wilkinson (Chemicals) Ltd. Fred Wilkinson had thus been actively engaged for nearly 70 years in the chemical industry, and he was one of the few remaining men who had dealt with chemicals and allied products from the very early days of the establishment of this industry in the West Riding of Yorkshire.

Fred Wilkinson's activities, however, extended over a wide range of interests. He took an active part in the political life of Bradford, and, from 1920 to 1926, he represented Tong Ward on the Bradford City Council and for a time he was Deputy Chairman of the Gas Committee. He was also a founder and a former President of the Tong Unionist Club, a founder of the Bradford East Division Conservative Association, of which he was a Vice-chairman, a Vice-president of the Bradford Conservative and National Liberal Association, and President of the Tong Allotments Association. It is not surprising to learn that he helped annually at the Tong Ward Old Folk's Treat.

Fred Wilkinson had a quiet and friendly manner, and he delighted to entertain his friends at the County Conservative Club. The writer, who had the privilege of his friendship for the greater part of fifty years, can testify to the efforts with which he endeavoured to emulate his father, not only in scientific interests but also, unostentatiously, in acts of good will towards his fellow men. Fred in his turn earned the tribute, paid earlier to his father, that he was the type of English gentleman one loves to meet, and that whenever any good action had been done anonymously in the district, he had been accused of doing it.

The end was typical of the man—he was at the club at lunch time, talking animatedly as usual, and next day he passed from our midst—one of Nature's finest gentlemen. He leaves a widow and two sons, to whom we offer our deep and sincere condolences.

HERBERT H. HODGSON

New Books and Publications

Artificial Fibres

By R. W. Moncrieff. 2nd edition 1954. Pp. xii + 455. London: National Trade Press Ltd. Price, 30s. 0d.

The author is to be congratulated on his revision of this book. The supplementary information which he has given in order to bring the reader up to date and to make good the deficiencies and omissions present in the first edition (reviewed in J.S.D.C., **67**, 151 (1951)) has been carefully written.

More attention has been paid to dyeing methods and to the blending of staple fibres, and a chapter has been added to deal with the economic and social aspects of fibres, including both the man-made and the natural fibres. Consequently there are 37 chapters in the new edition compared with 30 in the first edition, and the new edition is about half as large again (455 pages compared with 313). Thus the increase in price of 5s. 0d. is fully justified.

Like the first edition, the book is in five parts, dealing respectively with the structure and properties of fibres, regenerated cellulosic and alginic fibres, regenerated protein fibres, synthetic fibres, and processing.

It is unfortunate that in certain lists of dyes the author has confined himself to those of one manufacturer: in a future edition *Colour Index* numbers might be given, so that the reader can look up the names of equivalent dyes produced by other manufacturers also.

A final suggestion for the next edition may not meet with either the author's or the editor's approval, as it concerns changing the title of the book to *Man-made Fibres* instead of using the word "artificial", which has an unfortunate connotation, implying inferior.

H. A. THOMAS

Detergency Evaluation and Testing

By J. C. Harris. Pp. x + 210. New York and London: Interscience Publishers. 1954. Price, $3.75.

The never ending multiplication of detergent products—a recently published list enumerates one thousand—makes it more than ever essential to be able to obtain a reliable estimate of their efficiency. Furthermore, it is necessary to examine their behaviour at different concentrations and temperatures, in solutions of different pH values and containing different alkalis, other "builders", and sodium carboxymethyl cellulose, in order to determine the optimum conditions of use. The only practicable method is to employ laboratory tests, for the time factor alone precludes carrying out trials on a plant scale, which, furthermore,

requires a large expenditure of labour and materials. Nevertheless, it is important that results of laboratory tests should correlate with those obtained under practical conditions of operation.

It is therefore appropriate that the publishers of Interscience Manuals have included in the series a book dealing with the laboratory evaluation of detergents. The methods described are those which, over a period of many years, the author has found useful for separating potentially useful surface-active agents from those of less value.

It may not be necessary to carry out a full examination; preliminary tests may show a product to have undesirable properties, bearing in mind the projected use to which the agent is to be put. Such tests are described in the second chapter, and include tests for stability towards acids, alkalis, and metallic ions, for solubility in alkalis and in organic solvents, and for dispersion of lime soaps. The measurement of wetting, rewetting, and foaming powers is dealt with, but the section dealing with the measurement of surface and interfacial tensions is inadequate, and other sources would need to be consulted for more information.

The book then goes on to deal fairly extensively with laboratory techniques for evaluating the efficiency of detergents as regards cotton washing, the methods described being all those of American workers. The preparation of standard soiled fabric is described, but there is no mention of recent work which has shown the desirability of imitating more closely the composition of the actual dirt occurring on the articles to be washed in practice. Various washing machines are described, including the Launder-Ometer, the Terg-O-Tometer, and the Deter-Meter. Further important omissions occur in the section dealing with reflectance measurements. It would have been helpful if the relationship between reflectance and weight of pigment dirt had been more clearly brought out. It is also important to realise that the oily component of the soiling mixture may not always be removed in the same proportion as the solid component, and hence in addition to carrying out reflectance measurements, it may be desirable to determine residual oil in the washed material by a suitable extraction method.

Other subjects covered include washing procedures for wool and other fibres, hard surface cleaning, the use of radioactive isotopes in detergency investigations, and miscellaneous tests for brightening agents, pH, and corrosion. There is also a brief mention of the use of statistical methods.

The author has collected together in this small book a quantity of information which otherwise is not readily available, as it is scattered throughout the literature, and he has produced a most useful manual for workers in this field.

R. E. Wagg

Oils, Fats and Waxes

By C. Griffiths. Pp. 90, with 12 illustrations in text. London: Scientific Publications (Great Britain) Ltd. 1954. Price, 10s. 6d.

This book is an enlarged reprint of a series of articles in *Scientific Lubrication*, and it deals briefly with the most important properties of the saponifiable fatty products, with some mention of industrial products derived from them by chemical treatments—e.g. oxidised and sulphated oils, fatty acids, etc.—and with outlines of manufacturing processes. It is written, quite admittedly, from the lubrication expert's point of view, and does not treat topics such as surface-active products and their manufacture, or drying-oil chemistry at any great length.

It is essentially a book of facts. It gives brief information about the source, isolation, and purification of each of the chief vegetable, animal, and marine animal products with comments on their common uses. There are many tables giving the fatty-acid composition of the natural products and also the chief analytical constants. There are also concise but quite workable directions for the determination of these constants by methods which form the routine of a typical oils and fats testing laboratory.

The constitutional features of oils, fats, and waxes are dealt with in rather bare outline, but a final chapter, entitled "Recent Advances in the Chemistry of Oils and Fats", takes matters a little further, summarising recent work on the chromatographic separation of glycerides and of free fatty acids in mixtures, and work by Hilditch on the structure of naturally occurring triglycerides.

There is a short bibliography covering analytical methods and recent investigations.

Within the limits the author has set for himself, he has done a competent piece of work.

H. A. Turner

This Family Business

Pp. iii + 59. Leeds: Benjn. R. Vickers & Sons Ltd. 1954. No price.

The History of Price's of Bromborough 1854-1954

Pp. iii + 43. No price.

The first of these books commemorates the 125th year of the firm's existence, the other, as its subtitle indicates, the more conventional centenary. Apart from their obvious relation in the world of fatty acids, these two books have something very marked in common: each tells the story of a family business that has been built on the twin foundation stones of humanitarianism and sound business principles.

In the case of Vickers, particularly, a course of action prompted by humanitarian reasoning was so often shown subsequently to have been a good stroke of business that a cynic might well question the original motives; the religious outlook of all the generations of Vickers, however, is shown by the records to have been deep-rooted and very genuine.

The first part of *This Family Business* recaptures vividly the atmosphere of early nineteenth-century Leeds, when St. John's Church stood amidst open fields. This firm of textile oil merchants and processors has, indeed, been a family affair from the start, and its progress has been due to traditional characteristics that have been transmitted from one generation to the next. One of the many

lessons to be learnt from this book is that important inventions can be conceived by those who are not expert engineers and technologists.

Price's of Bromborough, reputed to be the largest manufacturers of fatty acids in Western Europe, take us from the days when tallow and palm oil were the normal raw materials for the making of candles, through the period of the use of stearine for this purpose, to the present time; today candles, being made almost exclusively from paraffin wax, are no longer a product of Bromborough, which specialises in the making of chemicals and distillates originating from oils and fats. Price's principal products—textile oils, oleines, stearines, fatty acids, and fatty alcohols—are used as raw or process materials on woollen, worsted, cotton, and rayon goods, for lubricating oils and greases, typewriter ribbons, stencils, emulsifying agents, soaps, fine chemicals, cosmetics, and very many more commodities.

It is interesting to read that the French textile industry was using oleine at the time of the Great Exhibition of 1851, but that it was corroding their spinning machines; they were soon converted to the use of Price's oleine distilled with steam, but it was apparently a harder task to persuade British industry that the new oleine was harmless to machinery and could replace the traditional olive oil. Of Bromborough's output of oleine, 65% now goes to the British wool and rayon industries, and the older method of separating stearic from oleic acid by hydraulic pressing has been superseded by a solvent separation method. This process is continuous and labour-saving, and gives improved products.

Both these books provide some fascinating glimpses of the past. It is abundantly clear, too, that both of these firms are well aware that the history of the future begins today.

H. LEMON

Manufacturers' Publications and Pattern Cards

The Society does not accept any responsibility with regard to the statements in the following notes. Any publication abstracted may be referred to by members of the Society on application to Dr. C. B. Stevens, Dyeing Department, Leeds University

Badische Anilin- und Soda-Fabrik

NEOPALATINE DYESTUFFS—This card contains dyeings in three depths on wool cloth of a new range of 9 pre-metallised dyes; 18 mixture dyeings are also included. They are recommended for dyeing wool in all forms, particularly where good levelness and fastness to wet treatments is required. They exhibit maximum levelling power in the presence of 3–4% sulphuric acid and 1–3% Uniperol W, an auxiliary product developed for use with this class of dye, particularly when deep dyeings are required. If a lower degree of levelness and fastness to rubbing is permissible, the sulphuric acid may be replaced by formic or acetic acid, while 3 members of the range may be dyed neutral. The lowest fastness to light quoted is 6, while the fastness to washing (Method "C") is 4 or better and to alkaline milling (Method "A") 4–5 or 5.

The Clayton Dyestuffs Co.

CIBACET DYES ON "TERYLENE" POLYESTER FIBRE APPLIED IN HIGH TEMPERATURE–PRESSURE DYEING MACHINES—This card contains dyeings on staple fibre (3 denier, 4 in. staple) in three depths of 6 disperse dyes and 15 mixture dyeings based on them. Dyeing is commenced at 50–60°C., and the temperature raised to 125°C. and maintained for 20 min., after which dyeing is complete. The dyeings are of average fastness to light and very good fastness to wet and chemical treatments. They do not sublime at 170°C. and thus withstand dry heat setting and permanent pleating at this temperature, which is the average for such processing.

Compagnie Française des Matières Colorantes

HELIASOL KHAKI 3R; HELIASOL OLIVE R—The two dyes described in this circular are anthraquinonoid vat dyes recommended for dyeing cotton and viscose rayon, and may be applied on the jigger, by pigment padding, and to packages in circulating-liquor machines. Fastness figures include—*Heliasol Khaki 3R:* Light 6, washing 4–5, chlorine 2. *Heliasol Olive R:* Light 5–6, washing 4–5, chlorine 2.

Courtaulds Ltd.

SPUN-DYED SERACETA—This booklet contains full information on the fastness properties of a range of spun-coloured acetate rayon yarn which includes 25 Standard and 14 Extra Bright colours. Of the standard range, 10 have a light fastness which is considered to be high enough for them to be equated in this respect with the vat dyes on cellulosic fibres. In addition to the actual fastness data, information is appended concerning particular features of individual colours, and details are given of the methods of assessment employed.

Farbenfabriken Bayer

ACRAMIN RED VIOLET FR EXTRA CONC.—This is a concentrated form of Acramin Red Violet FR, yielding prints of similar fastness but considerably clearer in hue.

INDANTHREN BRILLIANT PINK BL—This vat dye gives bright bluish pinks of very good fastness to light and wet treatments on cellulosic materials and is recommended for direct printing, particularly on curtain and finishing fabrics and dress goods. It may be discharged white without using Leucotrope W, and is also suitable for coloured discharges and coloured resists under aniline black and Anthrasols. Fastness figures on cotton include—Light 7, washing (at 95°C.) 4–5, chlorine 5.

Imperial Chemical Industries Ltd.

TECHNICAL INFORMATION LEAFLETS—These describe either the properties and applications of new auxiliary products, particular uses of existing products, or matters related to the application and the uses of particular dyes or the production of certain types of coloured effects. They would appear to be a means of supplementing information already published in technical circulars or pattern cards. Generally the title of the leaflet indicates its nature and scope.

Rubber No. 1. Vulcatard A—A New Retarder of particular use in Furnace Black Stocks.

Rubber No. 3. Vulcafor EFA.

Rubber No. 4. Vulcabond MR—A Rubber-to-metal Bonding Agent.

Rubber No. 6. Vulcafor BT.

Rubber No. 7. Notes on Transparent and Translucent Rubbers.

Rubber No. 14. Cellular Butadiene–Acrylonitrile Rubbers—This leaflet deals specifically with the compounding of cellular synthetic rubbers based on butadiene–acrylonitrile, e.g. Polysar NP 450 and Hycar OR–15.

The following leaflets are concerned with dyeing and printing—

No. 161. The Stability of Direct Dyes when dyed on Viscose Rayon at High Temperatures above 100°C.—The dyes have been classified in three groups. Group I are stable at high temperature under neutral dyeing conditions and exhibit considerable resistance when dyed under alkaline conditions. Group II also are stable at high temperature when dyed neutral, but are adversely affected

by alkaline conditions. Group III are unstable under both neutral and alkaline conditions. A further table shows the effect of adding various alkaline salts to the dye solution when dyeing Durazol Blue G 200 at 120°C. on viscose rayon.

No. 162. The Production of White and Illuminated Discharge Effects on "Terylene" Polyester Fabrics.

No. 167. The Use of Fixanol P in the Dyeing of Bast Fibres— Aftertreatment of direct dyeings on sisal, coir, and jute often substantially improves their fastness to water without significantly affecting the hue and the fastness to light. Dyeings of acid dyes also are improved, but the dyeing becomes weaker and the fastness to light is reduced.

No. 166. The Application of Duranol Inhibitor CF Paste by Dyeing and Padding.

No. 173. The Effect of Duranol Inhibitor CF Paste on the Shade and Light Fastness of Direct Dyestuffs— Of the 59 dyes examined, with only 5 was any significant effect on the hue of dyed viscose rayon observed, and in no case was any effect on the light fastness noted.

Dyehouse No. 178. Rubbing Fastness of Azoic Dyestuffs on Viscose Rayon— The best method of ensuring maximum fastness to rubbing is to prevent surface deposition of pigment during coupling. This pamphlet describes methods devised to that end.

Dyehouse No. 187. Fixanol P in the Dyeing of Spun Rayon Piece Goods for Crease-resist Finishing— The relative merits of a crease-resist finish with and without treatment with Fixanol P prior to crease-resisting have been determined in respect of the fastness to washing and to light of the dyeings.

Dyehouse No. 188. Aftertreatment of "Terylene" Polyester Fibre with Dispersol VL or Lubrol W— This leaflet replaces the Technical Information Note of 6 Aug. 1952 and Technical Information No. 130. It describes the use of these two products as antistatic agents.

Dyehouse No. 191. The "Back Tanning" of Nylon to improve the Fastness Properties of Water Soluble Dyestuffs— The recommended processes entail either treatment of the dyed material successively in solutions of tannic acid, tartar emetic, and stannous chloride or a simpler two-bath process in which tannic acid and tartar emetic only are used. Results for a few typical acid, direct, and Solacet dyes are given.

Dyehouse No. 192. Pad–Jig and Pad–Winch Application of Direct Dyestuffs to Spun Viscose Rayon Piece Goods— This replaces Technical Information Note No. 121.

Dyehouse No. 199. Dyestuffs for Tinting Cotton, Viscose Rayon, Acetate Rayon, Nylon, "Terylene" Polyester Fibre and Silk— Dyes and a suitable scouring treatment are suggested for each individual fibre. Specific recommendations must be sought for fibre mixtures.

Dyehouse No. 201. The Fastness of Disperse Dyes on Nylon to Pleating and Setting Treatments— The fastness of nylon dyed to a medium depth with a wide range of disperse dyes has been determined using (1) steam in an autoclave at outer and inner pressures of 30 and 15 lb./sq. in., respectively, for 20 min. and dry heat at 200°C. with a fabric-metal contact time of 10 sec. A supplementary set of results using dry heat at 215°C. for 20 sec. illustrates the importance of setting temperature and time. On the basis of the results obtained a range of the 11 most suitable dyes has been selected.

Dyehouse No. 202. Colour in School Buildings— Pigment combinations are recommended for producing the 46 colours of the Achrome (Munsell) range.

Dyehouse No. 204. The Fastness of Carbolan and Coomassie Dyestuffs dyed by the Carbolan Salt A Method to S.D.C. No. 2 Wash Test— Dyeings of a range of forty dyes have been produced in 1% depth (4% for navies and 8% for blacks), and figures are given for dyebath exhaustion and fastness to S.D.C. Washing Test No. 2 (Wool).

Chlorazol Union CFN Dyestuffs— This card contains dyeings on worsted cloth with cotton effect threads of a range of ten Chlorazol Union CFN dyes and six direct dyes suitable for shading purposes. They have been selected for dyeing faded wool garments by a one-bath union dyeing method in the presence of Lissapol N, the use of which promotes covering of the faded portion. They possess good colour value, cover cotton stitching well, and are economical and suitable for use in standing baths. Details of application and the fastness properties of the dyeings are appended.

Coomassie Bordeaux B— This acid dye gives bordeaux of good fastness to light and wet treatments on wool and Ardil protein fibre. It is of interest for dyeing loose stock, slubbing, and yarn, mixtures of wool and cellulosic fibres or nylon, and also tin-weighted and unweighted silk. Viscose rayon may be printed using the urea process. Dyeings on wool, unweighted silk, and nylon may be discharged to a good white. Fastness figures on wool include— Light 5, washing (repeated mild, 5 times at 40°C.) 3–4, perspiration (neutralised pattern) 3–4.

Soledon Pink 2B— This solubilised vat dye is particularly recommended for printing cotton and viscose rayon to give bluish reds of very good fastness to light and wet treatments. It may be applied by either the nitrite, thiocyanate, or chromate–acid age process, and can be used alongside Brentogen, mordant, and pigment dyes and Alcian Blue 8G; white resists are readily obtainable. Fastness figures for a print on cotton include— Light 6–7, washing (repeated severe, 5 times at 100°C.) 4, hypochlorite ("dry-chemicking") 5.

Solochromate Fast Brown G— This chrome dye gives greenish browns and is particularly suitable for application to loose wool and slubbing by the single-bath method. It is also of interest on Ardil, nylon, and unweighted silk. Fastness figures on wool dyed by the chromate method include— Light 6, alkaline milling 4–5, washing (repeated mild, 5 times at 40°C.) 5.

Solochromate Fast Red 6G— Yellowish reds of very good fastness to light and wet treatments may be obtained on loose wool, slubbing, yarn, and cloth. It is particularly recommended for application by the single-bath method. It is suitable for dyeing Ardil and unweighted silk. It is of slight importance for direct printing. Afterchrome dyeings on wool and silk are of some interest for white and coloured discharges. Fastness figures for a dyeing on wool by the chromate process include— Light 6–7, alkaline milling 3, washing (repeated mild, 5 times at 40°C.) 4.

Solochrome Brilliant Red 3B— This chrome dye gives particularly bright bluish reds and is recommended for use alone and in mixtures on loose wool, slubbing, stripped rags and shoddy, yarn, and cloth. It may be applied by all three methods, but maximum colour value is obtained by dyeing afterchrome. Level dyeings are obtained on tippy wool. It is also suitable for dyeing Ardil protein fibre and wool–Ardil mixtures, and is of some interest on nylon. Fastness figures for an afterchrome dyeing on wool include— Light 5, alkaline milling 4, washing (repeated mild, 5 times at 40°C.) 5.

The Surface Dyeing of Cellulose Plastics— This Technical Circular describes in detail suitable methods for dyeing cellulose acetate and nitrate plastics. Aqueous dyebaths are preferred, as no fire or toxicity hazards are involved, although dyeing takes longer and greater control, particularly of temperature, must be exercised. Figures are given for the fastness to light of dyeings on both types of material produced by recommended procedures.

The Mass Coloration of Cellulose Acetate, Polystyrene and Polythene Moulding Materials— This Technical Circular outlines the properties considered most desirable in the finished product and then details methods of assessing these. The methods of colouring and of subsequent testing are described for each type of plastic, and data are given for fastness to light, heat stability, ease of dispersion, colour, and transparency in respect of each member of a range of dyes suitable for each material.

Sandoz Products Ltd.

Omega Chrome Orange PML: Metomega Chrome Orange PML— This chrome dye is recommended for use alone and in mixtures for dyeing wool in all forms by either the afterchrome, on-chrome, or chrome mordant method. Dyeings are slightly redder than those obtained with the ML brand and are faster to potting. It is also of particular interest for Vigoureux printing and is suitable for dyeing polyamide fibres. Fastness figures for a dyeing on wool by the afterchrome method include— Light (daylight) 7, alkaline milling (severe) 4–5, potting 4–5.

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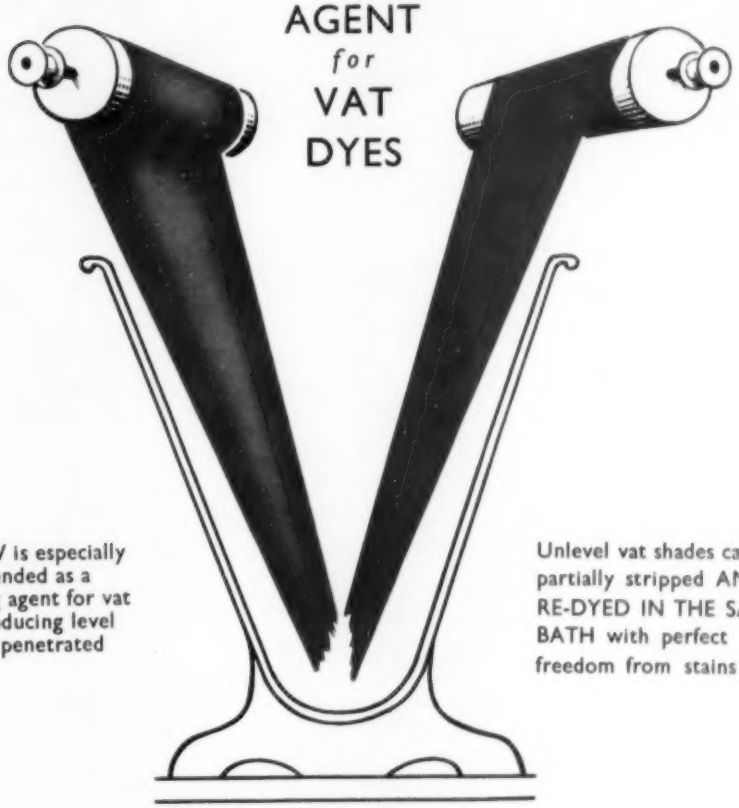

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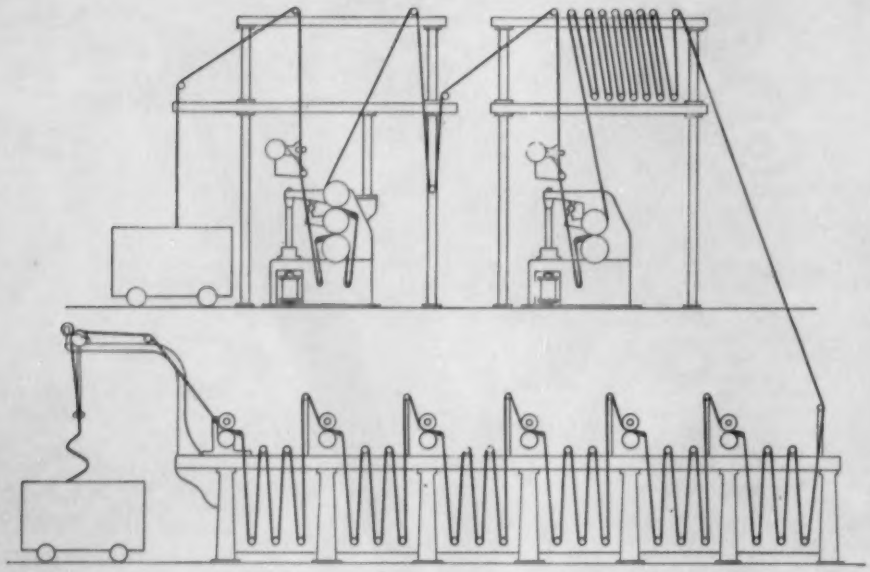

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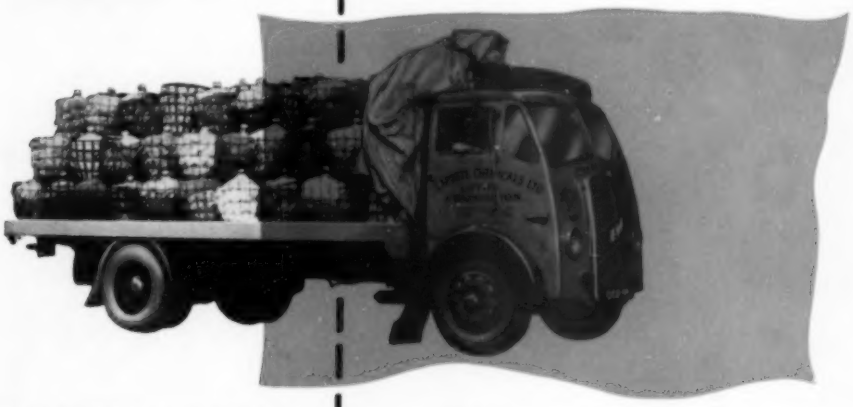

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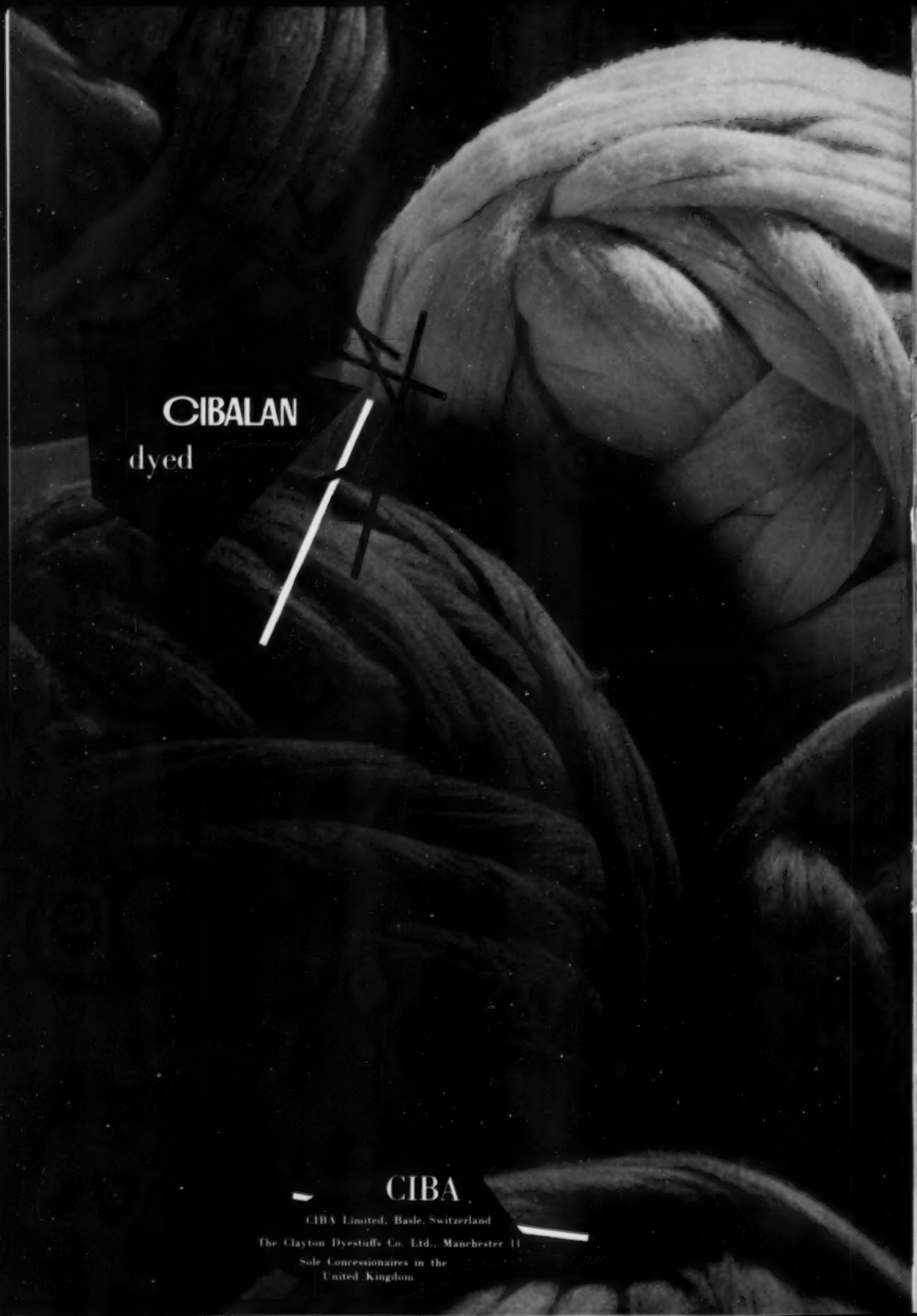
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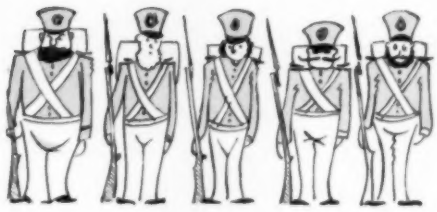
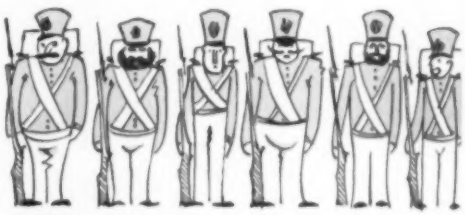

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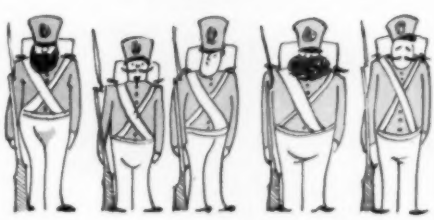
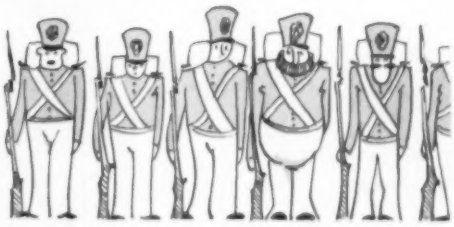

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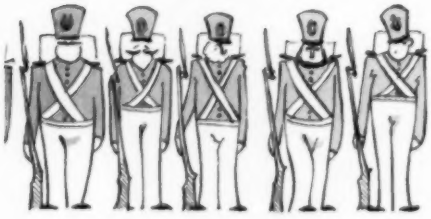
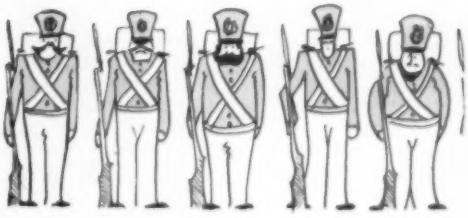

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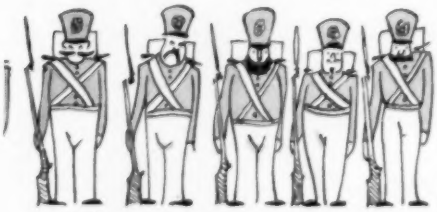
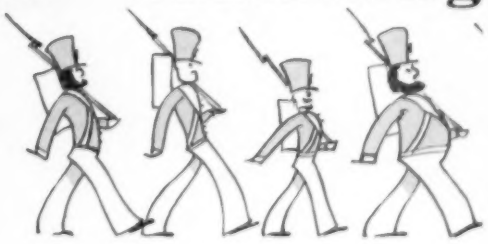

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The bodice and the skirt are of velvet adorned with gold embroidery. The oversleeves, which are lined with embroidered satin, reach almost to the ground, and each is tied about one-third of the way down above the wrist. The handkerchief (panuelo) is decorated with Spanish cut-work.

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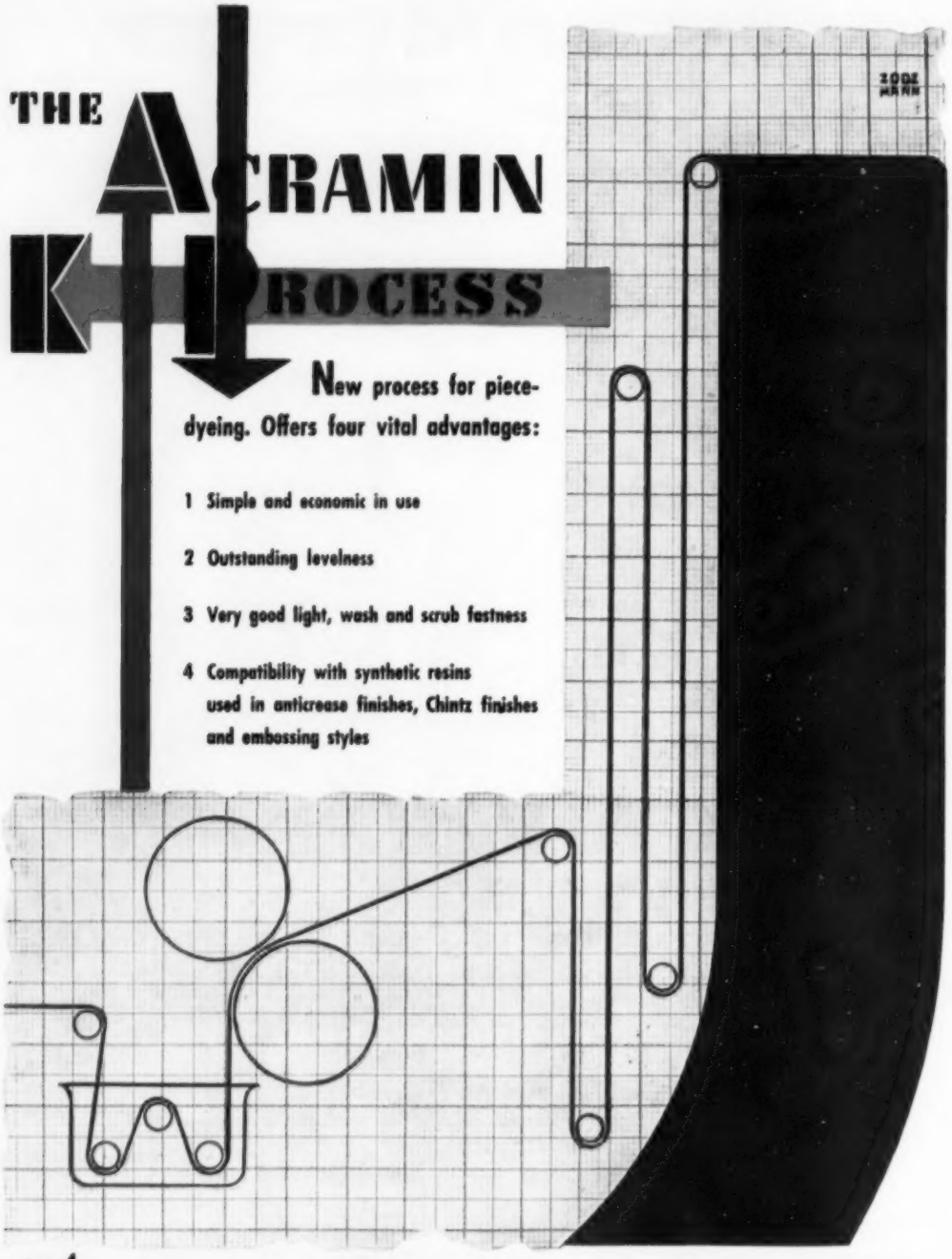

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Abstracts from British and Foreign Journals and Patents

The titles of abstracts may be modified. Abbreviations of names of firms are listed in J.S.D.C., **68**, *23 (Jan. 1952), and also, together with symbols and the periodicals abstracted, in the annual index*

I— PLANT; MACHINERY; BUILDINGS

Glass Heat Exchanger. F. Fröhlich. *Textil-Rund.*, **9**, 307–309 (June 1954).

Stated to reduce heat requirement by a 33–50% in conditioning, sizing, stentering, etc. Glass had advantages which outweighed its low heat conductivity. H. E. N.

Washing Machine. J. Nowotny. *Melliand Textilber.*, **35**, 416–417 (April 1954).

The machine ("System Karl Menzel", Maschinenfabrik, Bielefeld) requires little space but has a high performance. In the bath, between the cloth running in full width over guide-rollers, are displacement bodies, from which liquor is ejected turbulently against the material in such a way as to aid in keeping the piece opened out, and the liquor returns to them *via* an outlet in the bottom of the bath and a pump. H. E. N.

PATENTS

Oil Burner for producing Furnace Black. Phillips Petroleum Co. *BP* 711,816

An improved oil burner for a carbon black furnace. C. O. C.

Apparatus for producing Furnace Blacks. Columbian Carbon Co. *BP* 711,312

Simplified apparatus in which a hydrocarbon is decomposed by rapidly and uniformly mixing it with a hot gas at above the decomposition temperature of the hydrocarbon. C. O. C.

Rotary Mixer or Stirrer more especially for Paints. R. H. Mapp and R. S. Hill. *BP* 711,653

An improved mixer or stirrer comprises a centre shaft carrying at least one undulated disc, the crests and the troughs of the waves extending radially. The underside of this disc or of the lower disc if there is more than one, is provided with scrapers extending radially from near the centre shaft to the periphery of the disc. Preferably the periphery of the disc has a "sine-wave" form. C. O. C.

Producing Relative Movements between a Liquid and Articles in it. Ultrakust-Gerätebau Dr. Ing. Oswald Raudszus. *BP* 710,713

A simple, sturdy and compact device for producing sonic frequency vibrations in liquid by a magnetically vibrated agitator. C. O. C.

Treating Loose Fibres. Dexdale Hosiery Mills. *BP* 709,494

The material is placed in a chamber where it is successively and repeatedly exposed to the alternate action of suction and a gas. The machine is suitable for setting crimp imposed in nylon staple or tow. C. O. C.

Opening of Matted or Felted Fibres during Drying. H. Haas. *BP* 711,042

The compressed wet fleece of fibres is subjected on one side alternately to suction and gaseous pressure across its width at successive places in its line of travel, and similarly on the other side to alternate gaseous pressure and suction. During its passage the fibres are held between permeable bands or belts which are far enough apart to allow for the fleece increasing in thickness as a result of the opening. The method is particularly suitable for crimped viscose rayon. C. O. C.

Coating the Cylindrical Surface or the Outside of Rolls, especially for Photo-mechanical Printing Rolls. Louis Schneider & Cie. *BP* 709,572

The roller is uniformly and continuously coated by placing it vertically into a receiver into which the coating composition is forced from below and later drained therefrom. Before the composition is drained off the drain pipe of the receiver is closed by nipping a flexible hose forming part of the drainage pipe, draining being commenced by suddenly removing the nip from the hose. C. O. C.

Cake Holder for Dyeing Apparatus. M. W. Reno and J. E. Dougherty. *USP* 2,648,214

Interlocking means for positively retaining the cake separators in working position. C. O. C.

Dye Liquor Dispensing Meter. U.S. Secretary of Agriculture. *USP* 2,647,663

The flow of liquor through the outlet is automatically controlled by movement of a buoyant shuttle to the outlet. The device is readily calibrated and adjusted to deliver a predetermined amount of liquid. C. O. C.

Package Drying. B. Thies. *BP* 712,656

In a drier in which hot air is blown through the packages maintaining the air under pressure in a direct circuit results in less time being needed for drying and also cheapens the process. C. O. C.

Control Assembly for Web Feeding Apparatus. Korthe Engineering Co. *BP* 712,316

Control means depending on either partial or complete breaking of the web or upon excessive bulging thereof. C. O. C.

Blowing Nozzles for Tenters etc. J. Dungler. *BP* 712,086

Nozzles which operate across the whole width of the material being treated. C. O. C.

Compressive Shrinking of Yarns and Fabrics. Rydboholms. *BP* 712,427

Apparatus for compressive shrinking of yarn and fabrics comprises an endless flexible and elastic band and two rollers supporting the band in tension and positively driven at different speeds. This results in the tension of the band being increased around the roller running the fastest and being decreased when it leaves this roller. A press block is placed above the point at which the band leaves the roller so that it forms a nip for yarn or fabric passing between it and the band. Material placed on that section of the band which is under increased tension is thus introduced into this nip where it is shrunk when the band relaxes. C. O. C.

Pile Fabric. Dunlop Rubber Co. *BP* 712,240

Pile fabric having a very even pile is produced by electrostatic deposition. C. O. C.

Screen Printing Machines. L. G. Dubuit. *BP* 712,131

The object to be printed is rotated in synchronism with the displacement of the screen. C. O. C.

Textile Printing Blanket Washing Equipment. Dewey & Almy. *USP* 2,648,088

When printing with oil-base colours using an endless waterproof blanket as the backing up element, the blanket is cleansed by applying solvent to it exactly in proportion to the surface area passing the application point in a unit of time. Solvent is prevented from lying on the blanket and the apparatus mists and spreads such a minute amount of solvent over the blanket that 5 gal. of solvent suffices for 16,000–18,000 yd. of a 42 in. wide blanket. This is done uniformly and independently of the speed the machine is being run at. C. O. C.

Coating Tubular Fabric and like Narrow Materials. Bentley–Harris Manufacturing Co. *USP* 2,647,488

Distribution of Supplies of Treating Liquors to a Battery of Laundry Washers or Similar Machines. United States Hoffman Machinery Corpn. *USP* 2,647,384

Garment Steaming or Finishing. American Laundry Machinery Co. *BP* 714,425

II— WATER AND EFFLUENTS

Application of Chlorine and Treatment of Textile Wastes. N. S. Chamberlin. *Amer. Dyestuff Rep.*, **43**, 389–391 (21 June 1954).

Chemical treatment of waste liquors is discussed, with particular reference to the use of chlorine. J. W. B.

Decomposition of Very Dilute Viscose Solutions by Sulphuric Acid. E. Treiber, T. N. Kleinert, and W. Wincor. *Melliand Textilber.*, **35**, 553–554 (May), 657–659 (June 1954).

Using ultraviolet absorption spectra, it is shown that addition of an amount of H_2SO_4 insufficient to neutralise all the free alkali has very little effect on very dil. viscose. If enough H_2SO_4 is added to react with all the free alkali and to liberate the weak acids present (CO_2, H_2S, ester-xanthic acid), the sodium trithiocarbonate decomposes in a few hr. even at 6°c. and an initial pH of 7·6. If the amount of acid is increased to the quantity equiv. to the alkali content of the viscose minus twice the amount of alkali required to form the cellulose xanthate, the latter persists even for 1–2 hr., but the turbidity gradually intensifies. If the amount of acid is increased to give an initial pH of 4·7, corresponding to the presence of Na_2SO_4, free cellulose-xanthic acid, and xanthate, the concn. of the last decreases slowly, falling by 42% in 23 hr. Addition of excess H_2SO_4 gives early pptn., and after 6 hr. the xanthate concn. has fallen to one twenty-fifth. Fresh sediment contains chemically bound xanthate groups, which slowly split off, liberating CS_2. This explains why in the liquor in contact with the sludge the concn. of H_2S falls progressively whilst that of CS_2 is maintained. When alkali comes into contact with sediment containing xanthate groups, a yellow or yellow-brown coloration is produced. Such colours are observed occasionally in plants treating effluent from viscose manufacture. H. E. N.

III—CHEMICALS; AUXILIARY PRODUCTS; FINISHING MATERIALS

Some Aspects of the Chemistry and Textile Uses of Sequestering Agents. J. V. Summersgill. J.S.D.C., **70**, 278–283 (July 1954).

Certain compounds which are capable of forming complexes with metals are potentially useful for the prevention of undesirable effects due to metals frequently encountered in textile processing. The nature of the reaction between such compounds and metals is discussed with reference to derivatives of iminodiacetic acid and complex phosphates. Some applications of these compounds in the prevention of troubles caused by calcium, magnesium, iron, copper, and some other metals are outlined. AUTHOR

Complexones. XXV—Formation Constants of Metal Complexes of Ethylenediaminetetra-acetic Acid and of 1:2-Diaminocyclohexanetetra-acetic Acid. G. Schwarzenbach, R. Gut, and G. Anderegg. *Helv. Chim. Acta*, **37**, 937–957 (June 1954).

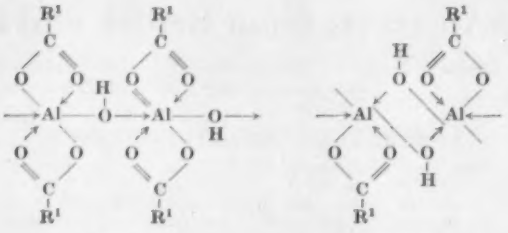
In mixtures containing the metal complex MY^{n-4} of ethylenediamine- or 1 : 2-diaminocyclohexane-tetra-acetic acid as well as the uncomplexed cation M^{n+}, it is usually possible to determine the concn. of the latter with an accuracy of 1% by means of a polarograph. Such measurements have been used for the determination of the ratio of the formation const. (K) of the complex of one metal to that of another, and from these ratios the individual K of 49 complexes have been obtained. The best values of K (20°c., ionic strength 0·1) of metal complexes are tabulated. H. E. N.

Annual Review of Literature on Fats, Oils, and Soaps—I and II. M. M. Piskur. *J. Amer. Oil Chem. Soc.*, **31**, 176–191 (May); 236–253 (June 1954).

A comprehensive review of the literature and patents on fats, oils, and soaps, including detergents. P. G. M.

Chemical Nature and Physical Properties of Aluminium Soaps. A. E. Alexander. *J. Oil & Col. Chem. Assocn.*, **37**, 378–382 (July 1954).

Heat of reaction studies in non-aqueous media, and the chemical analysis of soaps produced in organic and aq. media, indicate that tri-soaps do not exist as discrete chemical cpd. Di-soaps seem to exist, with formulæ $Al(OR)L_2$ and $Al(OH)L_2$, where R and L denote the alcohol and fatty acid radicals, from the anhyd. alkoxide and aq. reactions respectively. Mono-soaps may exist, but positive evidence is so far confined to limited infrared data reported by earlier workers. Formulæ are proposed for the mono- and di-soaps—



Di-soap Mono-soap

which agree well with the physical properties of these materials; this is discussed briefly. Peptising agents such as amines and pyridine break the Al–O co-ordinate links. Water acts to some extent as a peptiser, and an increase in the moisture content of a soap makes its soln. in organic media more fluid; addition of small amounts of water to soln. of soaps formed by the alkoxide method (in absence of water) causes a marked increase in viscosity, which indicates the formation of linear aggregates. J. W. D.

Surface-active Agents and their Far-reaching Influence in the Textile Industry. P. J. Sullivan. *Amer. Dyestuff Rep.*, **43**, P331–P334 (24 May 1954).

Equilibria between Urea and Formaldehyde in Aqueous Solution. A. Iliceto. *Ann. chim.* (Rome) **43**, 625–637 (1953); *Chem. Abs.*, **48**, 7404 (10 July 1954).

The equilibria between urea and HCHO were studied in dil. soln. at 20 and 35°c., unreacted HCHO being determined by the bisulphite method. The equilibrium constants K_1 and K_2 for the reaction urea $+CH_2(OH)_2 \rightleftharpoons$ (hydroxymethyl)urea + H_2O and (hydroxymethyl)urea + $CH_2(OH)_2 \rightleftharpoons$ bis(hydroxylmethyl)urea + H_2O were at 20°c. $K_1 = 1{\cdot}01 \times 10^3$, $K_2 = 1{\cdot}37 \times 10^3$; at 35°c. $K_1 = 0{\cdot}67 \times 10^3$, $K_2 = 1{\cdot}00 \times 10^3$. K_2 was constant while the ratio HCHO/urea was varied from 0·1 to 4 and the pH from 7 to 12. In conc. soln. (0·5 — 1M with respect to HCHO) $K_1 = 0{\cdot}85 \times 10^3$ at 20°c. For ratios HCHO/urea > 2, more than 2 mol. of HCHO reacted for each mol. of urea. Tris- and possibly tetrakis(hydroxymethyl)urea are formed. Presence of the tetrakis compound could not be shown because even at HCHO/urea = 20 only 2·81 mol. of HCHO react with 1 mol. urea. The heats of formation of the mono-, bis- and tris(hydroxymethyl)ureas are 4·90, 3·76 and 2·27 k.cal. C. O. C.

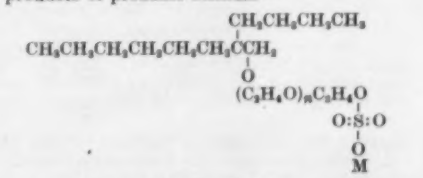
PATENTS

Detergent. Monsanto. *BP* 713,128

A mixture of (*a*) a condensate (15–30 parts by wt.) of ethylene oxide (0·5–2·3) with abietic acid (1) and (*b*) a water-soluble alkali metal poly- and/or, pyro- and/or ortho- and/or hexameta-phosphate and (*c*) starch and/or carboxymethyl cellulose is an excellent detergent which does not yield too much foam. C. O. C.

Hydroxy Ether Sulphates of High Surface-activity. Monsanto. *USP* 2,647,913

The condensates of 3–11 moles of ethylene oxide with 1 mole of 2-butyloctanol-1 when sulphonated and neutralised yield products of probable formula—



(m = 3–5; M = alkali metal or NH_4) have excellent wetting and detergent properties. C. O. C.

Acidic Detergent—Stain Remover. Chemische Fabrik Budenheim. *BP* 712,327

A mixture of diglycollic acid or acid alkali metal diglycollates with synthetic organic detergents is a good stain remover for textiles. C. O. C.

Stable Aqueous Hydrogen Peroxide. Buffalo Electro-Chemical Co. *BP* 713,156

Pyridine carboxylic acids are excellent stabilisers for aqueous hydrogen peroxide of any strength. C. O. C.

Chromium Co-ordination Complexes of Saturated Perfluoromonocarboxylic Acids as Water Repellent Coating Agents. Minnesota Mining & Manufacturing Co. *BP* 712,784

The chromium complexes of saturated perfluoromonocarboxylic acids of 4–10 C are solid, slightly soluble in water and very soluble in alcohol or acetone and so differ from the ordinary Cr salts of these acids. They are produced by reacting chromyl chloride with the acid in presence of an inert anhydrous solvent and reducing, and, if desired, hydrolysing and ammonating the product. They can be used to produce extremely thin, greenish, firmly adherent, water repellent films on glass, metals, paper, textiles, cellulosic films, etc. The films as well as being hydrophobic are also oleophobic. C. O. C.

Flameproofing Compositions. Monsanto. *USP* 2,648,597

The flameproofing properties of the condensate formed by treating phosphorus oxychloride with ammonia at < 100°C., heating the product at 110–150°C., and freeing from NH_4Cl, are improved by treating it with a carboxylic acid of 2–4 C, preferably with acetic acid. C. O. C.

Tanning Agents. FH. *BP* 713,061

Brown tanning agents of 90% strength and which strike through rapidly are obtained by sulphonating a mixture of colophony and a naphthol, treating the product with a mononuclear phenol and then with formaldehyde. They have good tanning action at high pH and produce a well-plumped leather similar to bark-tanned leather.

BP 713,941

Similar products are obtained by sulphonating a mixture of colophony and a naphthol, treating the product with a phenol alcohol, if desired in presence of a free mononuclear phenol, and then with formaldehyde. C. O. C.

Alkyldiformylphenylenediamines—Solubilising Sulphuric Esters of Vat Dyes in Printing Pastes (IX p. 473).

IV—RAW MATERIALS; INTERMEDIATES; COLOURING MATTERS

Fluorescence. E. J. Bowen. *J. Oil & Col. Chem. Assocn.*, **37**, 264–267 (May 1954).

The origin of fluorescence is outlined, and the equation expressing its exponential decay with time is given and discussed. The quenching of fluorescence by (*a*) chemical reaction, e.g. of Fe^{2+}, Br^-, or I^- with fluorescent dyes in soln., and (*b*) internal electronic energy conversions, e.g. the appearance of triplet luminescence at low temp., is dealt with in greater detail. J. W. D.

Dichroism of a Dye Molecule and some Benzene Derivatives. L. V. Smirnov. *Izvest. Akad. Nauk S.S.S.R., Ser. Fiz.*, **17**, 695–698 (1953): *Chem. Abs.*, **48**, 6825 (25 June 1954).

All dye molecules contain chains of conjugated bonds; therefore, the properties of spectra in the region 200–800 mμ are determined by the structure of the π-electron spectrum. The values of optical d. $D_{||}$ and $D_{\perp}$ depend on the orientation of the molecule and on the angles formed by the electronic oscillators with the structural axis. Dichroism indicates the degree of anisotropy of the π-electron system. Absorption spectra with polarised light or dichroism measurements of solutions of Auramine, Congo Red, Methylene Blue, Crystal Violet, Parafuchsin, Aurine, trimethoxyaurine, *p*-toluidine, *m*-nitrophenol, *p*-nitrophenol, *p*-aminophenol, and *p*-nitrosodimethylaniline, are given and discussed. Symmetrical triphenylmethane dyes have dichroism values different from the theoretically expected zero. C. O .C.

Studies of Tautomerism. III—Nitrosation Products of *m*-Chlorophenol. A. Kraaijeveld and E. Havinga. *Rec. Trav. chim.*, **73**, 537–548 (July 1954).

The two products of nitrosation of *m*-chlorophenol first reported by Hodgson *et al.* (*J.C.S.*, **123**, 2499 (1923); **131**, 1553 (1929); **133**, 1494, 2227 (1931); 520 (1937); and 1808 (1939)) have been re-examined. The higher-melting product (m.p. 184°c.) is shown to be an equilibrium mixture of the two tautomers (3-chloroquinone 4-oxime and 3-chloro-4-nitrosophenol), whilst the lower-melting product (m.p. 142°c.) is an addition complex of equimolecular proportions of the higher-melting product and 3-chlorobenzene-6-diazo-oxide (m.p. 124°c.). The components may be separated chromatographically from chloroform over alumina. A. J.

Studies on Tautomerism. IV—Complexes of 3-Halogenobenzene-6-diazo-oxides with Quinone Monoximes (Nitrosophenols) and some other Complexes. A. Kraaueveld and E. Havinga. *Rec. Trav. chim.*, **73**, 549–558 (July 1954).

The product of m.p. 142°c. formed during the nitrosation of *m*-chlorophenol in neutral or weakly acidic medium has been further investigated, and its structure as an addition complex of equimolecular proportions of 3-chlorobenzoquinone 4-oxime and 3-chlorobenzene-6-diazo-oxide is supported by analytical data, by its formation from the components, by its behaviour during recrystallisation, and by X-ray data. The diazo-oxide is thought to arise during nitrosation owing to formation of the 6-nitroso compound and diazotisation of this by the nitrous acid used for nitrosation. The presence of the 4-diazo-oxide in the nitrosation products has also been shown. The nitrosation of *m*-bromophenol gives completely analogous products. A. J.

Effect of Boron Trifluoride on the Orientation of the Nitro Group in the Nitration of Phenol and Aniline. A. V. Topchiev, V. P. Alaniya, and G. S. Shnaider. *Doklady Akad. Nauk. S.S.S.R.*, **95**, 89–92 (1 March 1954).

Much *meta* substitution occurs when the equimolecular complexes formed by BF_3 with phenol and with aniline are nitrated. The phenol complex, treated with 20% nitric acid, yields *o*-, *m*-, and *p*-nitrophenols in the proportions 63 : 32 : 5 approx.; and the aniline complex, treated with a conc. nitration mixture, yields *o*-, *m*-, and *p*-nitroanilines in the proportions 13 : 67 : 20 approx. A. E. S.

Dimethylation of Primary Aromatic Amines by means of Formaldehyde. B. M. Bogoslovskii. *J. Gen. Chem. U.S.S.R.*, **24**, 922–924 (May 1954).

The reaction of formaldehyde in 100% formic acid with the three nitroanilines is studied, and it is shown that, by the use of these reactions, *NN*-dimethyl-4-nitroaniline, 4:4′-bisdimethylamino-2:2′-dinitrodiphenylmethane, and 4:4′-diamino-3:3′-dinitrodiphenylmethane can be prepared in good yields. A. E. S.

Oxidation of *N*-Alkylanilines and Related Components with Benzoyl Peroxide. J. T. Edward. *J.C.S.*, 1464–1467 (May 1954).

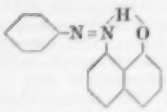
Aromatic monoalkylamino compounds are oxidised with benzoyl peroxide in equimol. quantities in benzene at 0°c. to give the corresponding *o*-benzamidophenols. Yields are low, but the simplicity of the reaction and the ease of isolating the phenol will commend the method. The following amines are treated—*N*-methyl-, *N*-propyl-, *N*-butyl-, *N*-*iso*pentyl-, *N*-benzyl-, and *p*-chloro-*N*-methyl-aniline, *N*-methyl-*o* (and *m* and *p*)-toluidine, *N*-ethyl-α-naphthylamine, and 1:2:3:4-tetrahydroquinoline. After 20 min. (or overnight for *p*-chloro-*N*-methylaniline) the phenol is extracted with dil. aq. NaOH. Equally good yields are obtained in $H{\cdot}CO{\cdot}NH_2$ or $CHCl_3$, but lower in $(C_2H_5)_2O$. *N*-Methylanthranilic acid resists attack. H. H. H.

Influence of Substituent Groups on Nuclear Reactivity in the formation of Substituted Diphenyls through Reactions of Aromatic Diazo and Cognate Compounds with Aromatic Liquids. III—Substitution of Nitrobenzene by the *p*-Anisyl Radical. O. Simamura and T. Migita. *Bull. Chem. Soc. Japan*, **27**, 228–231 (June 1954).

The decomp. of *N*-nitroso-*p*-acetanisidide in nitrobenzene at room temp. yields 4-methoxy-4′-nitrodiphenyl and 4-methoxy-2′nitrodiphenyl in a ratio of 1 : 1·6. From the result of a similar experiment in a mixture of nitrobenzene and benzene, which compete for the *p*-anisyl radical produced from *N*-nitroso-*p*-acetanisidide, the relative reactivities of the *ortho*, *meta*, and *para* positions of nitrobenzene towards the *p*-anisyl radical were found to be 7·24, 0, and 8·95 respectively, the reactivity of one nuclear position of benzene towards the same radical being taken as unity. Full details of the work are given. J. W. D.

Azo Dyes from 1:5-Aminonaphthol and some of its Derivatives. IX—Hydrogen-bonding in certain *peri*-Hydroxyazo Dyes. V. V. Perekalin and Z. S. Segalina. *J. Gen. Chem. U.S.S.R.*, **24**, 683–687 (April 1954).

Although there is little doubt that certain properties distinguishing *o*-hydroxyazo dyes from the corresponding *p*-hydroxyazo dyes (low alkali-solubility, absorption max. independent of pH of medium) are to be attributed essentially to the presence in the former of hydrogen bonds, the possibility remains of the existence of the dye in the quinone hydrazone form, which has also been advanced as an explanation of these properties. The behaviour of 8-phenylazo-1-naphthol—



(I)

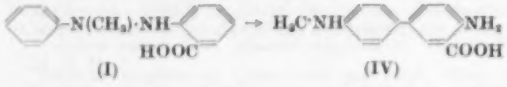
and its derivatives, in which such isomerisation is impossible, is now shown to be closely parallel to that of the *o*-hydroxyazo dyes with respect to these properties, and it is considered that they contain a hydrogen bond (as shown). However, I and derivatives of I that do not contain a suitable group in the 7-position, unlike *o*-hydroxyazo dyes, do not form metal lakes. I is prepared, for the first time, by diazotising 4-phenylazo-1:5-aminonaphthol (II) and then replacing the diazo group with hydrogen. The *peri*-hydroxyazo dyes examined were I, II, and 1-phenylazo-2:8-aminonaphthol. A. E. S.

Substituted Benzidines and Related Compounds as Reagents in Analytical Chemistry. XIII—Behaviour of certain *N*- and *NN'*-Alkylated Benzidines towards Oxidising Agents. R. Belcher A. J. Nutten, and W. I. Stephen. *J.C.S.*, 2543–2545 (July 1954).

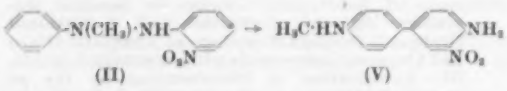
N-Methyl-, *NN'*-dimethyl-, and *NN'*-tetramethyl-benzidine and the corresponding ethyl deriv. are more sensitive towards oxidising agents (MnO_4^-, VO_3^-, $Cr_2O_7^{2-}$, Fe^{3+}, $S_2O_8^{2-}$, IO_3^-, IO_4^-, ClO^-, BrO_3^-, $Fe(CN)_6^{3-}$, and Cl_2) than are the simple diamines, and afford highly coloured stable products. In dil. acetic acid the colours are greenish blue for the monoalkyl-, greenish yellow for the dialkyl-, and bright yellow for the tetra-alkyl-benzidines; the colours of the ethyl deriv. are less intense. In mineral acid, all the amines give bright yellow oxidation products. Their applicability as redox indicators is discussed. H. H. H.

Rearrangement of Some *N*-Substituted Hydrazobenzenes. G. R. Clemo and T. B. Lee. *J.C.S.*, 2417–2419 (July 1954).

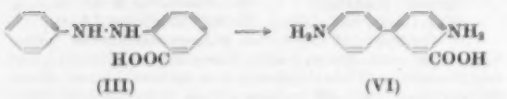
The transformation of hydrazobenzenes of the type $Ar{\cdot}N(CH_3){\cdot}NH{\cdot}Ar^1$ ($Ar \neq Ar^1$) has not hitherto been investigated, and the rearrangements of the hydrazobenzenes (I), (II), and (III) to the benzidines (IV), (V), and (VI) are now found to be readily effected by warm dil. HCl).



(I) (IV)



(II) (V)



(III) (VI)

H. H. H.

Aromatic Azo Compounds. VI—Action of Light on Azoxy Compounds. G. M. Badger and R. G. Buttery. *J.C.S.*, 2243–2245 (July 1954).

A number of azoxy deriv. are isomerised to *o*-hydroxyazo deriv. by exposure to light, the O atom migrating from N to the further nucleus; an intramol. mechanism is proposed. Chromatographic analysis has shown that the supposed red "isomers" of 1:1'- and 2:2'-azoxynaphthalene are respectively mixtures of unchanged material with 2-hydroxy-1:1'-azonaphthalene and with 1-hydroxy-2:2'-azonaphthalene. H. H. H.

Hydrogen Bonding in Naphthol AS Compounds (Azoic Coupling Components) from Infrared Spectroscopy. H. Hoyer. *Kolloid Z.*, **133**, 7–11 (Oct. 1953).

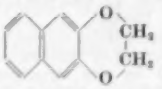
The infrared absorption spectra of unassociated molecules of the Napthol AS class of compounds (2-naphthol-3-carboxyanilides) have been studied in the region of the fundamental X–H valence vibration frequency. Molten hexachlorobenzene was used as a solvent because of the sparing solubility in other suitable solvents. In these solutions the compounds do not exist in the lactim but in the lactam form with the internal hydrogen bond between the hydroxyl and the oxygen of the peptide group. Absorption spectra are given from 2·5μ to 4·5μ for alizarin and seven Naphthol AS compounds in hexachlorobenzene and for naphthalene in carbon disulphide. L. P.

Utilisation of Benzene Hexachloride Isomers other than the γ-Isomer. III—Synthesis of Several Azoic Dyes and their Application. S. Kato and K. Obayashi. *J. Chem. Soc. Japan Ind. Chem. Sect.*, **55**, 117–118 (1952): *Chem. Abs.*, **48**, 7305 (25 June 1954).

2:4:5-Trichloroaniline, 5:2:4-chlorodimethoxyaniline, 5:2:4-chlorodiethoxyaniline and 4-chloro-6-nitro-1:3-diaminobenzene were prepared from the non-effective isomers of benzene hexachloride and their use as azoic developing components studied by coupling each with 3-hydroxy-2-carboxynaphthalene. C. O. C.

Naphthodioxan (2:3-Dihydronaphtho[2,3]*p*-dioxin), Some Derivatives and Azo Dyes—I. P. M. Heertjes, A. M. ter Horst, and J. M. Persijn. *Rec. Trav. chim.*, **73**, 513–528 (July 1954).

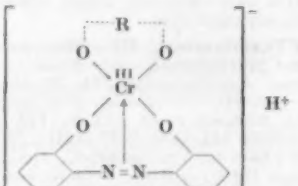
Naphthodioxan (I) is prepared from 2:3-dihydroxynaphthalene by the action of KOH in ethylene glycol or 2:3-butanediol followed by refluxing with ethylene dichloride. The product is separated by vacuum distillation and recrystallisation from ethanol. Sulphonation with chlorosulphonic acid below 5°c. yields the 5-sulphonic acid. Sulphuric acid (sp. gr. = 1·84) at 150°c. yields chiefly the 7-sulphonic acid and below 150°c. a small amount of the 6 acid. Nitration in glacial acetic acid at 20°c. gives chiefly 5- with smaller amounts of 6- and 7-nitronaphthodioxans.



(I) A. J.

Metal-complex Dyes without Sulphonic Acid Groups. H. Pfitzner. *Melliand Textilber.*, **35**, 649–651 (June 1954).

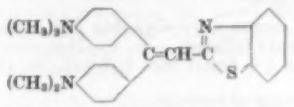
A short review with 27 references in which are mentioned Cibalan (Ciba), Irgalan (Gy), Lanasyn (S) dyes, and a new class, Neopalatine (Basf) dyes of general formula—



where R is introduced from a colourless complex-forming compound (*GP* 846,142). S. R. C.

Dyes derived from Michler's Ketone and Heterocyclic Compounds containing Active Methyl or Methylene Groups. G. M. Oksengendler and A. I. Kiprianov. *Ukrain. Khim. Zhur.*, **16**, 383 (1950): *Chem. Abs.*, **48**, 1683 (10 February 1954).

The synthesis of a series of dyes from Michler's ketone, thioketone or Auramine and various heterocyclic compounds containing active CH_3 or $>CH_2$ groups is described. Among the heterocyclic compounds used were 2-methylbenzthiazole and its methoxy, nitro and phenyl derivatives, 2-methylbenzoxazole, 3-ethylrhodanine and 1-phenyl-3-methyl-5-pyrazolone. A typical example is the preparation of a red, the methiodide of—



by heating 2-methylbenzthiazole and Michler's ketone in acetic anhydride. R. K. F.

Optical Properties of Colloidal Dye Solutions. M. V. Savost'yanova. *Izvest. Akad. Nauk S.S.S.R., Ser. Fiz.*, **17**, 747–755 (1953): *Chem. Abs.*, **48**, 6827 (25 June 1954).

Mie's formulæ for the optical properties of systems of small particles are simplified. By introducing the complex index of refraction $m = n - i\,x$ (x = absorption coefficient) calculations are made from Fuchsin-benzene and gold-water. The simplified formulæ agree well with Mie's more complete expressions. The coefficient of extinction of light K in Fuchsin-benzene solution has a maximum which shifts and flattens towards longer wavelengths when particle size increases from < 20 to 200 mμ. Experimental data show a maximum for K at 500 mμ. This shift is caused by a different spectral response of the coefficient of the formula and their relative importance, depending on particle size. The sols were made by adding a few drops of dye solution to a liquid in which the solvent is soluble but the dye is not (e.g. a CCl_4 solution of Fuchsin added to benzene). The sols contain some dissolved dye but the curve for the colloidal particles can be obtained if the spectral curve for the dye solution is subtracted from the total curve. The maximum is close to the absorption maximum of the solid dye; thus the colour of the solutions resembles the colour of the dye. C. O. C.

Action of Light on some Organic Colouring Matters —I and II [Triphenylmethane Dyes]. C. M. Desai and B. K. Vaidya. *J. Indian Chem. Soc.*, **31**, 261–264, 265–268 (March 1954).

I— The oxalates of Crystal Violet, Malachite Green, and Brilliant Green on exposure to sunlight for periods up to 20 days in aq. soln. and in the solid state yield Michler's ketone and *p*-diethyl- and *p*-dimethyl-aminoazobenzene respectively. Crystal Violet affords also some leuco base. Rosaniline is only slightly affected after 33 weeks' exposure. The photodecomposition products show a ketone band.

II— The four dyes of Part I were exposed to the following light sources— (i) quartz–mercury arc, (ii) C.P.A. glass-enclosed carbon arc, (iii) 1000-c.p. Point-o-lite lamp, and (iv) sunlight. The absorption spectra of the exposed dyes show that the same decomposition products (cf. Part I) are obtained with each light source, but in different proportions at different rates. A. J.

Fluorene Analogues of Triphenylmethane Dyes; Calculation of their Light Absorption by the Molecular-orbital Method. D. A. Brown and M. J. S. Dewar. *J.C.S.*, 2134–2136 (June 1954).

The fluorene analogues of crystal violet and of malachite green (two isomers) were observed by Barker and Barker (*J.C.S.*, 1307 (April 1954)) to absorb at much lower frequencies than do the parent triphenylmethane dyes. Calculation of the light absorption of these compounds by the L.C.A.O. molecular-orbital method now shows that these shifts can be ascribed quantitatively to the effect of forming the additional C–C bonds. There appears to be no need to postulate non-planarity in the fluorene ring. H. H. H.

Influence of the Addition of High-molecular Electrolytes upon the Absorption Spectra and Fluorescence of Organic Dyes— II and III. N. Mataga and M. Koizumi. *Bull. Chem. Soc. Japan*, **27**, 194–197, 197–200 (June 1954).

II— Addition of potassium polyvinyl sulphate (PV8K) to soln. of Pyronine G brings about changes in the absorption spectrum of the dye. With dye concn. $< 2 \times 10^{-4}$ M. no change occurs even when a large excess of PV8K is added. At concn. $> 4 \times 10^{-4}$ M. a metachromatic band appears which becomes stronger as the PV8K concn. increases; there is a corresponding decline in the strength of the α- and β-bands. There is a critical concn. of PV8K above which the metachromatic band is suppressed, the α- and β-bands recovering until the original form of the spectrum of pure Pyronine G is almost resumed. At still higher concn. of dye the change in form of the spectrum is more pronounced, whilst the recovery is delayed to a much higher PV8K concn. and is greatly reduced in extent. In a theoretical discussion these effects are interpreted quant. in terms of changes in aggregation of the dye ions. Experimental details are given in full.

III— The effect of additions of Na and K alkyl sulphates of different chain lengths upon the absorption spectra and fluorescence intensities of various basic dyes has been studied. Changes in absorption spectra brought about by the addition of electrolytes with only one functional group may be directly correlated with changes in dye ion aggregation. In contrast to substances with many functional groups (e.g. PV8K) some specific aggregation or orderly array of the added electrolyte ions appears to be necessary. This structure is considered to be quite labile, and spectral changes bear a delicate relationship to the aggregation of dye ions, the orderly array of electrolyte ions and the interaction between dye and electrolyte ions. The observed effects are discussed fully, and an account is given of the effect of such factors as the chain length of the alkyl sulphate, the dye concn., and the temp. J. W. D.

Organic Phosphorescence I. S. Kato and M. Koizumi. *Bull. Chem. Soc. Japan*, **27**, 189–194 (June 1954).

The phosphorescence decay curves of Trypaflavine in various concn. on filter paper have been measured. It would appear that the triplet state is little affected in concn. quenching. The experimental work and the mathematical treatment are given in some detail. J. W. D.

Preparation of Quinaldine Derivatives from Aromatic Amines and Vinyl Ethers. B. A. Porai-Koshits, L. S. Efros, V. N. Vertkina, and V. V. Lutsenko. *J. Gen. Chem. U.S.S.R.*, **24**, 895–898 (May 1954).

Some quinaldine derivatives can be prepared, with advantage, from readily available vinyl ethers and aromatic amines. Thus, butyl vinyl ether and aniline, in presence of nitrobenzene and conc. HCl, give quinaldine itself; and the 6-methyl, 8-methoxy, and 6- and 8-nitro derivatives are prepared by use of the corresponding substituted anilines. Yields vary from 25 to 50%. *m*-Nitroaniline, *m*-phenylenediamine, and aminophenols do not react. A. E. S.

Near-ultraviolet Absorption Spectra of some Heterocyclic Compounds. I— Benzoxazoles. R. Passerini. *J.C.S.*, 2256–2261 (July 1954).

The ultraviolet absorption spectra up to 210 mμ. have been reported for benzoxazole and several mono- and di-substituted deriv., the substituents being CH_3, C_6H_5, NO_2, SR, and NR_2 (where R = H, Alk, Ar, or acyl). Interpretations are suggested on the basis of essentially localised chromophores, with resonance interaction between them in suitable structural circumstances. H. H. H.

Near-ultraviolet Absorption Spectra of some Heterocyclic Compounds. II— Benzothiazoles. A. Cerniani and R. Passerini. *J.C.S.*, 2261–2264 (July 1954).

The work of Part I (cf. preceding abstract) is supplemented by a similar study of benzothiazole and its deriv., with corresponding interpretation on resonance theory. A general bathochromic shift without intensification from benzoxazole to benzothiazole compounds, which is found in the bands assigned to the benzo-ring chromophore, is

attributed to a shift of relative conjugating power of O and S from the order O > S in the ground state of the C $2p\pi$ shell, towards the order O < S, as the $2p\pi$ shell becomes enlarged in electronically excited states.

H. H. H.

Some Halogen-substituted Carbocyanine Dyes. N. Bregant. *Arhiv Kem.*, **23**, 188–191 (1952): *Chem. Abs.*, **48**, 6887 (25 June 1954).

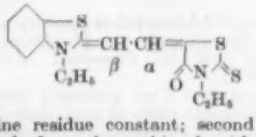
The reaction product of anilinehydrochloride and S_2Cl_2 (*GP* 360,690; 367,344) was made alkaline and treated with acetone and sodium-2-amino-5-chlorothiophenol by Beilenson and Hamer's method to yield 6-chloro-2-methylbenzothiazole (I). This with C_2H_5I gave 6-chloro-2-methyl-3-alkylbenzothiazolium iodide (II). II (0·04 mole) was dissolved in anhydrous pyridine (100 c.c.) at 100°c. and cooled to 60°c. To this solution was added CH_3COCl (0·08 mole) over 15 min. The mixture was replaced at 100–110°c. for 12 hr., the pyridine renewed by vacuum distillation, and the residue suspended in 80 c.c. of water made alkaline with K_2CO_3, and finally extracted with ether. The extract was dried with K_2CO_3, the ether removed by vacuum distillation and the residue recrystallised from alcohol to give a 40·3% yield of 2-(acetylmethylene)-3-ethyl-6-chlorobenzothiazole. 2·48 g. of this were re-refluxed at 160°c. for 1 hr. with 3 g. of 2-methyl-3-ethylbenzothiazolium iodide. After cooling the product was filtered, washed with ether, dried at 90°, and recrystallised from methyl alcohol to yield 16·3% of the dye 6-chloro-3:3′-diethyl-9-methylthiacarbocyanine iodide. Equivalent amounts of I and p-CH_3-C_6H_4-SO_2CH_3 were heated for 6 hr. in a sealed tube at 120°c. to yield 6-chloro-2-methyl-3-ethylbenzothiazolium p-toluenesulphonate. A 15% solution of this in anhydrous pyridine was refluxed for 1 hr. with 2 moles of ethylorthoacetate. While hot the mixture was treated with twice its volume of 40% aq. NH_4Br. This mixture was poured into ten times its volume of water, stood for 12 hr. at 0°c., the ppt. filtered, dried and recrystallised from methyl alcohol to give a 15% yield of 6:6′-dichloro-3:3′-diethyl-9-methylthiacarbocyanine bromide. The absorption spectra of the latter and of IV gave nearly parallel curves with absorption maximum at 545 and 550 mμ respectively. C. O. C.

Synthesis of a 1:3-Dioxo*iso*indoline Carbocyanine Dye. N. Bregant. *Arhiv Kem.*, **23**, 192–4 (1952): *Chem. Abs.*, **48**, 6889 (25 June 1954).

1-Chloro-3-phthalimido-2-propanone (4·64 g.) in absolute alcohol (50 c.c.) was refluxed 3 hr. with thioacetamide (1·3 g.), cooled, poured into aq. $NaHCO_3$ (300 c.c.), filtered, washed with water and dried to give a 78% yield of 2-methyl-4-(phthalimido methyl)thiazole. This (3·4 g.) was heated in a sealed tube with C_2H_5I (4·5 g.) at 120°c. for 8 hr., the product boiled in petroleum ether and recrystallised from absolute alcohol to give an 85% yield of 2-methyl-4-(phthalimidomethyl)-3-ethylthiazolium iodide. Of this 2 g. was refluxed 10 min. with anhydrous, freshly distilled pyridine (50 c.c.), $CH(OC_2H_5)_3$ (4 c.c.) added, refluxed 1 hr. at 160°c. with occasional shaking, cooled, poured into cold water (250 c.c.) and stood overnight at 0°c. to give a 12% yield of the dark violet prisms of bis-2-[4-(phthalimidomethyl)-3-ethylthiazole]trimethincyanine iodide. C. O. C.

***mero*Cyanine Dyes derived from Rhodanine. VI—Dimethin *mero*Cyanines containing an Alkyl or Phenyl Group in the Polymethin Chain.** M. V. Deĭchmeister, Z. P. Sytnik, I. I. Levkoev, and É. B. Lifshits. *J. Gen. Chem. U.S.S.R.*, **24**, 898–905 (May 1954).

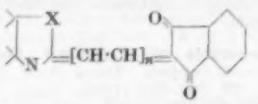
A study is made of the effect on the absorption spectra of substitution of CH_3, and in some cases also C_2H_5 and C_6H_5, in the α-, and in some cases β-, position of *mero*cyanines such as—



(3-ethylrhodanine residue constant; second heterocyclic residues derived from benzothiazole (shown above), benzoxazole, 4-phenylthiazole, 6-dimethylaminobenzothiazole, naphtho[1,2]thiazole, benzoselenazole, and thiazoline). Substitution of CH_3, C_2H_5, or C_6H_5 in the α- or β-position of the benzothiazole and benzoxazole dyes leads to bathochromic shifts in the absorption max. The bathochromic shift (> 13 mμ.) resulting from substitution of CH_3 in the α-position falls as the basic character of the variable heterocycle (and therefore also the polarity of the dye) increases, and it passes over into a hypsochromic effect for the dye derived from 4-phenylthiazole. It is considered that the effect of the electron-donating methyl group is to level out the electron density in the less basic dyes, in which there is only a small shift of electrons within the chromophore from the nitrogen towards the carbonyl, and to accentuate the unlevel electron distribution in the more basic dyes. A. E. S.

Colour of some *mero*Cyanine Dyes derived from Indane-1:3-dione. V. G. Zhiryakov and I. I. Levkoev. *J. Gen. Chem. U.S.S.R.*, **24**, 710–717 (April 1954).

*mero*Cyanines of formula—



(n = 1, 2, and 3; X = $C(CH_3)_2$ or S) are prepared by condensation of indane-1:3-diones, suitably substituted in the 2-position, with quaternary salts of (*a*) 2:3:3-trimethyl*pseudo*indole, (*b*) 2-methylbenzothiazole, and (*c*) 2-methyl-4:5-diphenylthiazole, and their absorption spectra are determined in ethyl alcohol and compared with those of the corresponding series of symmetrical mono-, tri-, and penta-methin cyanines and oxanines (the tri- and penta-methin oxanines have been synthesised for the first time). The *mero*cyanines have absorption max. (mμ.) at (*a*) 495, 588, 684; (*b*) 506, 596, 706; (*c*) 520, 611, 722 (for n = 1, 2, and 3 respectively in each case). The cyanines have max. (mμ.) at (*a*) 546, 634, 746; (*b*) 558, 654, 763; (*c*) 588, 683, — (for mono-, tri-, and penta-methin dye in each case). The mono-, tri-, and penta-methin oxanines have max. (mμ.) at 459, 551, and 650. The results are analysed as in previous papers of this school (cf. J.S.D.C., **67**, 122 (1951); **68**, 220 (1952)). The hypsochromic shift from the mean of the values for the corresponding symmetrical dyes is very small, and the wavelength increment from n = 1 to n = 2 is less than from n = 2 to n = 3; both of these facts point to a relatively even distribution of electron density throughout the system. The low polarity of these *mero*cyanines is confirmed by the smallness of the changes observed in their absorption spectra when measured in a series of mixtures of methyl and decyl alcohols, which are considered to provide a range of solvents that are of varying polarity, but consist entirely of molecules of similar chemical characteristics (the use of water–pyridine mixtures for this purpose by Brooker *et al.* (see J.S.D.C., **68**, 73 (1952)) is deprecated, since this condition does not hold). A. E. S.

Light Absorption and Constitution of *mero*Cyanines. M. Coenen and M. Pestemer. *Z. Elektrochem.*, **57**, 785–795 (1953): *Chem. Abs.*, **48**, 7431 (10 July 1954).

A study of the absorption in the visible and ultraviolet regions of molecules containing conjugated double bonds in a chain, with auxochromic N atoms and antiauxochromes, CN or COR at opposite ends. CN and COOR gave approx. the same bathochromic shift. $:C(CN)_2$ and $:C(CN)(COOR)$ show similar spectra; introduction of $C(COOR)_2$ gives a bathochromic shift as does increase in length of the polymethin chain. Polymethin chains substituted in the 2 and 3 positions prefer a "boat" form and give simpler and higher absorption bands than do unsubstituted chains. The CN group has an inductive but no mesomeric effect. 38 dyes were examined. C. O. C.

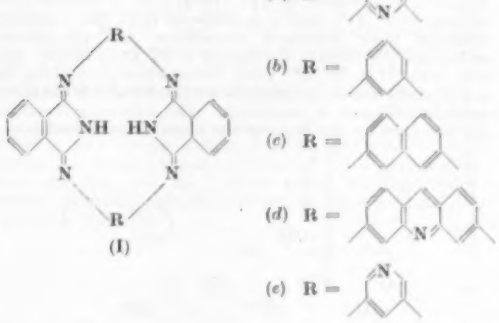
Temperature-dependent Colour Changes in some *mero*Cyanines. Y. Hirshberg and E. Fisher. *J. Chem. Phys.*, **22**, 572–3 (1954): *Chem. Abs.*, **48**, 7433 (10 July 1954).

Pronounced colour changes were seen when solutions of several *mero*cyanines were cooled to below room temperature. Spectrophotometric measurements showed that these colour changes were caused by changes in the relative intensity of two absorption bands. From the change with

temperature of the thermal equilibrium between the two modifications characterised by the two absorption bands, the energy difference between the two modifications was 2–3 k.cal./mole. C. O. C.

Conjugated Macrocycles. XXV—Cross-conjugated Macrocycles with Inner Great Rings of 16, 20, and 24 Atoms. P. F. Clark, J. A. Elvidge, and R. P. Linstead. *J.C.S.*, 2490–2497 (July 1954).

The condensation of 1:3-di-imino*iso*indoline with *m*-phenylenediamine, 2:7-diaminonaphthalene, and 2:8-diaminoacridine gives the respective macrocycles (I*b*, *c*, and *d*), which have 16-, 20-, and 24-membered inner great rings, and I*e* with 3:5-diaminopyridine. Unlike I*a*, and in keeping with their structures, the new macrocycles do not co-ordinate metals centrally, though I*e* forms insol. amorphous compounds with Cu and Ni acetates. Structures are discussed and compared with those of related linear compounds.



H. H. H.

Blue Phthalocyanine Pigments. I—Reaction Temperature and Time of Synthesis. M. Mori. *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **56**, 37–9 (1953): *Chem. Abs.*, **48**, 7913 (10 July 1954).

Phthalocyanine pigments were prepared by the Wyler method (*BP* 464,126: cf. J.S.D.C., **53**, 363 (1937)), with anhydrous $CuCl_2$ or anhydrous $FeCl_2$ at various temperatures between 150 and 250°C. and for times of reaction from 0·5–4·0 hr. Measurements by the Pulfrich photometer showed that the product produced at 200–220°C. with a reaction time of 4 hr. had the purest colour. Maximum yield 70%, was obtained at 250°C. with anhydrous $CuCl_2$ but the product lacked purity of colour. C. O. C.

Reduction of Anthraquinone and other Polycyclic Quinones with Aluminium Alkoxides (Meerwein–Pondorff Reagent). S. Coffey and V. Boyd. *J.C.S.*, 2468–2470 (July 1954).

The reaction between aluminium alkoxides and anthraquinones produces the corresponding anthracene, 9:10-dihydroxyanthracene, or 9:10-dihydro-9:10-dihydroxyanthracene, according to the alkoxide used and the experimental conditions. For example, amino- are first formed from nitro-anthraquinones, and these may react further with the products obtained from the oxidation of the alkoxide; 1-amino-2-methylanthraquinone affords 2:4-dimethyl-3-azabenzanthrone; 1:5-dichloroanthraquinone cannot be reduced beyond the dihydrodihydroxyanthracene stage; anthanthrone and flavanthrone are reduced to anthanthrene and flavanthrene respectively. H. H. H.

Amination of Anthraquinone with Hydroxylamine in Sulphuric Acid. A. C. Robson and S. Coffey. *J.C.S.*, 2372–2374 (July 1954).

The reaction between anthraquinone and hydroxylamine in hot conc. H_2SO_4 with $FeSO_4$ or V_2O_5 as catalyst affords a mixture, separated by chromatography, of 1- and 2-amino- and 1:4-, 1:5-, 1:6-, 1:7-, 1:8-, and 2:7-diamino-anthraquinone. Substitution occurs equally in the α or the β positions. V is more active than Fe^{2+}, but the reaction still occurs very slowly without added catalyst. H. H. H.

Cyclisation of Benzamido Derivatives of 1:1-Dianthraquinonylamine to Derivatives of 1:2-7:8-Diphthaloylcarbazole. W. Bradley and J. V. Butcher. *J.C.S.*, 2311–2314 (July 1954).

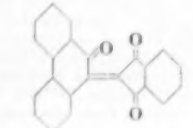
The 4:4′-, 4:5′-, and 5:5′-dibenzamido deriv. of 1:1′-dianthraquinonylamine are cyclised by heating with conc. H_2SO_4 to the corresponding dibenzamido deriv. of 1:2-7:8-diphthaloylcarbazole. Heating with H_3PO_4 provides a convenient means of hydrolysing many *N*-acylamino-anthraquinones. H. H. H.

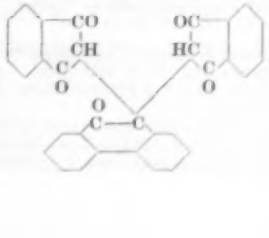
Direct Hydroxylation of Aromatic Compounds. W. Bradley. *Chem. and Ind.*, 631–633 (29 May 1954).

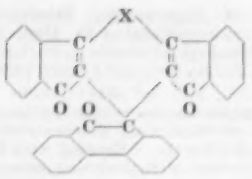
A review. The ease of direct substitution by OH depends principally on the degree of unsaturation of the nucleus; benzene, naphthalene, and anthracene are in the order of increasing ease of substitution by OH, as they are also for substitution by Br, NO_2, or SO_3H. The parent hydrocarbons do not undergo substitution, but they do so after conjugation with electron-attracting groups such as NO_2 or CO, the orientation of the incoming OH groups always being *ortho* or *para* to the former groups. Arylsulphonic acids yield, with KOH, phenols, the electron-deficient SO_3H group being replaced by OH. Carbonyl compounds whose nuclei are of low unsaturation, e.g. fluorenone, undergo elimination of the CO group; others, such as *meso*-benzanthrone, 5:6- and 7:8-benzo*meso*benzanthrone, and 6-phenyl*meso*benzanthrone, undergo direct hydroxylation *para* to the CO group. 3-Benzoyl*meso*benzanthrone gives both a hydroxy derivative and 3:8-dibenzopyrenequinone (involving a cyclisation reaction) on fusion with KOH and an oxidant. *amphi-iso*Pyranthrone undergoes dihydroxylation, and anthanthrone similarly gives the 3:9-dihydroxy derivative (even when 2:8- or 4:10-bromo substituents are present, these being eliminated). In all known instances monoketones yield monohydroxy derivatives, and diketones give dihydroxy compounds; this is due to the fact that once a OH group is introduced into a nucleus it forms a conjugated system with the CO group, and is consequently reduced in activity, so that only one of several possible isomers may be formed, e.g. with 1:8:9-naphthanthr-10-one. When associated with NH_2 groups, CO groups lose much of their characteristic reactivity; thus the direct hydroxylation of *peri*naphthalimide is much more difficult than that of *meso*benzanthrone. The case of acenaphtho[1,2-b]quinoxaline shows that hydroxylation of the nucleus occurs even under the comparatively slight stimulus of a C:N grouping in place of CO. Other instances of direct hydroxylation are cited briefly. J. W. D.

Condensation of Phenanthra-9:10-quinone with Indane-1:3-dione. G. Ya. Vanag and L. S. Geita. *Doklady Akad. Nauk S.S.S.R.*, **95**, 277–280 (11 March 1954).

In an attempt to prepare the substance I, phenanthra-9:10-quinone is condensed with indane-1:3-dione. The product, however, is II, a colourless substance that forms red enolates with strong bases. Compound II, when treated with acetic anhydride in presence of conc. H_2SO_4, yields a yellow substance (III, X = O), which is re-converted into II by hot alcoholic alkali. The yellow pyran deriv., when treated with ammonia or aniline, yields a red substance (III, X = NH or N·C_6H_5 respectively).





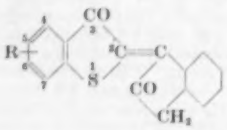


(III)

A. E. S.

Synthesis of Thioindoxyl. Condensation of some Thioindoxyls with 1:2-Diketoindane. J. N. Chatterjea and K. Prasad. *J. Indian Chem. Soc.*, **31**, 203–210 (March 1954).

Thioindoxyl is obtained in 20% yield by the action of HCl on the diazoketone obtained by the action of diazomethane on the acid chloride of thioaspirin. 5- and 7-methylthioindoxyl condense with 1:2-diketoindane in warm acetic acid containing catalytic amounts of HCl to give orange–red compounds thought to be I. With 5-chloro- and 5-bromo- and to a lesser extent with 7-chlorothioindoxyl, mixtures are obtained thought to be due to condensation with both carbonyl groups of 1:2-diketoindane.



A. J.

Sensitisation of the Internal Photoeffect of Semiconductors by Chlorophyll, Phthalocyanine, Haematin, and Allied Pigments. E. K. Putseiko and A. N. Terenin. *Doklady Akad. Nauk. S.S.S.R.*, **90**, 10005–10008 (1953): English translation issued as U.S. Atomic Energy Comm., NSF-tr-147, 5 pp. (1953).

Phototropy of Chlorophyll Solutions. R. Livingston, G. Porter, and M. Windsor. *Nature*, **173**, 485–486 (13 March 1954).

Degassed soln. of chlorophylls *a* and *b*, coproporphyrin-dimethyl ester, and phaeophytin *a* have been studied by means of flash spectra. The normal ground-state absorption of these pigments is almost completely absent when the spectrum is observed immediately after a photolytic flash; some new regions of absorption appear except in the case of phaeophytin *a*, soln. of the triplet state of which are almost opaque throughout the visible and near ultraviolet regions. Reduction of the intensity of the flash from 125 to 75 joules does not appreciably affect the photochemical effect, which is equally efficient in benzene and in methanol. Exclusion of water from soln. of chlorophyll *b* does not materially affect the formation of the triplet state, but saturation of the soln. with air virtually prevents it. The half-life of the principal photochemical transients formed in these experiments is $2–5 \times 10^{-4}$ sec. Four sets of spectra are reproduced to illustrate the discussion. J. W. D.

Fine Structure of Azulene. W. L. Galloway, D. H. Reid, and W. H. Stafford. *Chem. and Ind.*, 724 (19 June 1954).

Further evidence for the betaine-type structure for azulene, in which the seven-membered ring fulfils the cationic function, is given. Azulenes react similarly to pyridine and enol-betaines with acyl halides to form *C1*- or *C3*-acyl compounds with elimination of halogen hydracid. These are Friedel–Crafts reactions without the use of a catalyst. The carbonyl oxygen of the resulting acyl compounds is basic, as shown from spectral evidence.

A. J.

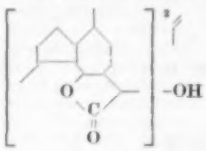
Separation of Pigment Cells of Cacao. H. B. Brown. *Nature*, **173**, 492 (13 March 1954).

Energy Transfer between Chromophore and Protein in Phycocyanin. T. T. Bannister. *Arch. Biochem. Biophys.*, **49**, 222–233 (1954): *Chem. Abs.*, **48**, 7093 (25 June 1954).

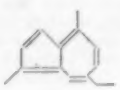
The efficiency with which light which is absorbed partly by the protein excites fluorescence of phycocyanin in pure solutions is the same as that of the light absorbed by only the chromophore portion of the phycocyanin molecule. About 46% of the absorption in the peak at 227 mμ. band of phycocyanin is attributable to absorption by the tryptophan and tyrosine of the protein; the chromophore contributes the remaining 54%. It seems that conversion of the ultraviolet excitation quanta of the protein into red quanta of the chromophore occurs in the phycocyanin molecule with the same efficiency as transformation of ultraviolet into red excitation quanta within the chromophore itself. The mechanism of this intramolecular transfer is probably similar to that of the intermolecular transfer responsible for the sensitised fluorescence of atoms or molecules (e.g. chlorophyll, a fluorescence sensitised by a carotenoid or phycobilin). C. O. C.

Chamazulene Precursor from Chamomile (*Matricaria chamomilla* L.). Z. Čekan, V. Herout, and F. Šorm. *Chem. and Ind.*, 604–605 (22 May 1954).

A cryst. precursor of chamazulene (II) has been isolated from *Matricaria chamomilla* L. by the method of Jung and Wendler (*Pharmazie*, **8**, 117 (1953)); it is termed pro-chamazulene (IV), and it is different from the precursor obtained from *Artemesia absinthium*, viz. pro-chamazulenogen (I). Steam distillation of IV from faintly acid soln. gives II in 70–75% yield, the reaction proceeding via a previously known intermediate (III), for which the name guaiazulenic acid is suggested. The following formulae are proposed on the basis of the experimental evidence—



(I)



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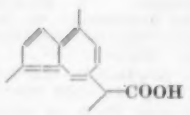

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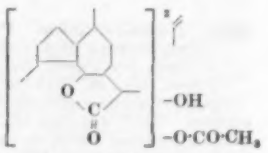


(IV)

The positions of the functional groups and double bonds in IV are now being determined. J. W. D.

Melanin Formation: Mechanism of the Oxidation of Tyrosine by Tyrosinase. D. Keilin. *Bull. Soc. Chim. biol.*, **35**, 993–1005 (1953): *Chem. Abs.*, **48**, 7077 (25 June 1954).

Mainly discussion; 22 references. C. O. C.

Structure of Melanin. J. L. Stoves. *Chem. and Ind.*, 580 (15 May 1954).

An amplification of an earlier communication (Idem, *ibid.*, 158 (1954)). J. W. B.

Colouring Matters of the Aphididæ. XI—Pigments from *Hamamelistes* Species. S. F. MacDonald. *J.C.S.*, 2378–2381 (July 1954).

The pigments of *Hamamelistes spinosus* Shimer and *H. betulae* Mordvilko are found to represent a new type of aphin series, and are converted enzymically into the same rhodoaphin, $C_{20}H_{22}O_{11}$, which appears to be a dihydroxy-erythroaphin containing a further O atom of unknown function. H. H. H.

Violet Pigment from the Mediterranean Medusa *Rhizostoma pulmo*. A. Christomanos. *Nature*, 173, 875–876 (8 May 1954).

A violet pigment is extracted by water at 2–4°C. from the subtentacles and marginal bodies of *Rhizostoma pulmo*. An amorphous violet residue is ultimately obtained which, from studies of the reaction with $SbCl_3$, of the decolorisation with H_2O_2, and of the spectrum, is considered to be a conjugated protein with a prosthetic group belonging, or relating, to the carotenoids. J. W. B.

PATENTS

1-Amino-6-fluoroanthraquinone. Ciba. *BP* 712,837

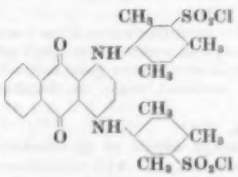
1-Amino-6-fluoroanthraquinone and mixtures of it with 1-amino-7-fluoroanthraquinone are prepared by heating 1-chloro-6-fluoroanthraquinone with a mixture of *p*-toluenesulphonamide, anhyd. sodium acetate and copper acetate in nitrobenzene at 170–175°c. for 2 hr. and then at 190–195°c. for 2 hr. followed by hydrolysing the resulting sulphonamide in H_2SO_4 at 60–65°c. for 40 min. The starting 1-chloro-6-fluoro derivative is made by sulphonating 2-fluoroanthraquinone in presence of Hg salt and treating the sulphonic acid with an alkali chlorate, as described in the following abstract. R. K. F.

1-Chloro-6-fluoroanthraquinone. Ciba. *BP* 712,889

2-Fluoroanthraquinone (by condensation of phthalic anhydride and fluorobenzene followed by cyclisation) is heated at 125–130°c. in oleum containing mercuric sulphate. After pouring into water containing a little $NaClO_3$, boiling and filtering, Na_2CO_3 is added and sodium 2-fluoroanthraquinone-5-sulphonate allowed to separate. It contains a proportion of the 2:7 isomer depending on the quantity of Na_2CO_3 used. The fluorosulphonates are converted to the corresponding fluorochloro compounds by treating with $NaClO_3$ in presence of HCl. R. K. F.

Arylaminoanthraquinone Sulphonyl Chlorides. Gy. *BP* 712,771

1:4-Diarylaminoanthraquinones which may carry methyl or ethyl groups attached to the aryl residues, and chlorine or bromine at positions 6 and/or 7, are treated with chlorosulphonic acid at −10 to 100°c. to give water insoluble sulphonyl chloride derivatives. Thus a compound of probable formula—



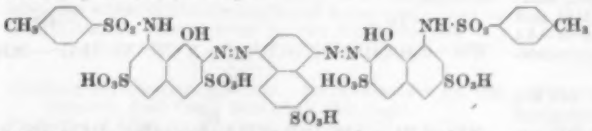
is prepared by treating 1:4-di-(2′:4′:6′-trimethyl)-phenylaminoanthraquinone with chlorosulphonic acid at 40°c. until a test sample is soluble in boiling 2% NaOH. It is separated by pouring the resulting mixture into ice and brine. R. K. F.

Blue and Blue-Green Disazo Acid Dyes. B. Gaspar and P. D. Dreyfuss. *USP* 2,612,496

Bright blue and blue-green dyes have the general formula—

Acyl·NH·A¹(OH)·N:N·B·N:N·A²(OH)·NH·Acyl

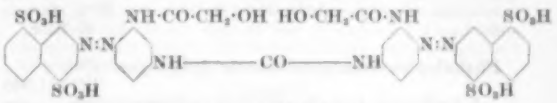
(A¹ and A² = naphthalene residues in which the OH is *ortho* to the azo link; B = an aromatic nucleus in which the two azo links are in the *para* position; B preferably contains 2 O·Alk groups *para* to each other, and A¹ and A² preferably are derived from mono- or di-sulphonic acids of 1:8-aminonaphthol). The fastness to light of such dyes depends largely on the acyl group, those derived from 2:4-dichlorobenzoyl-H acid, for instance, being faster than similar dyes derived from toluenesulphonyl-H acid. These preferred structures give dyes of desired spectral characteristics, do not diffuse or desensitise photographic emulsions, and give colourless reduction products in dye-bleaching processes of colour photography. Thus the nitro group of the monoazo compound 4-nitro-1-naphthylamine-6-sulphonic acid→*p*-toluenesulphonyl-H acid is reduced to NH_2 with Na_2S, and the resulting aminoazo compound diazotised and coupled with toluenesulphonyl-H acid to yield the disazo dye—



which gives blue-greens on wool and silk. A dry gelatin film containing this dye has a sharp absorption maximum at ca. 660 mμ. E. S.

Yellow Dischargeable Direct Cotton Disazo Dyes. FBy. *BP* 713,217

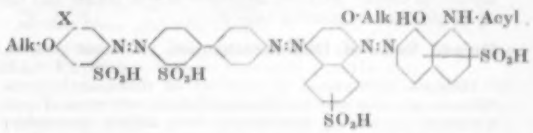
Two mol. of a monoazo compound arylamine→*N*-monoglycollyl-*m*-phenylenediamine are condensed with 1 mol. of phosgene to give urea derivatives which are yellow direct cotton dyes, superior in alkaline discharging properties to similar dyes containing *N*-acetyl instead of *N*-glycollyl groups. Thus, *m*-nitro-*ω*-chloroacetanilide is treated with alkali, or *m*-nitroaniline is heated with polyglycollide to ca. 150°c. in presence of a little H_2SO_4, to give *m*-nitroglycollanilide. Reduction of the nitro group then gives *N*-monoglycollyl-*m*-phenylenediamine. This is coupled with diazotised 2-naphthylamine-4:8-disulphonic acid in presence of acetic acid, and the amino-monoazo compound so formed condensed with phosgene. The product—



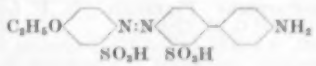
dyes cotton dischargeable reddish yellow. E. S.

Olive Green Direct Cotton Trisazo Metal(Copper)-complex Dyes. FBy. *BP* 712,868

The copper complexes of trisazo dyes—



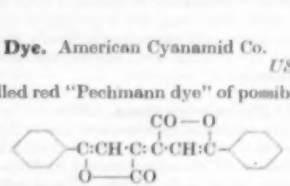
(X = H or Alk; Acyl = radical of a monocarboxylic acid) are olive green direct cotton dyes, faster to light than similar dyes containing the radical of 4:4′-diaminostilbene-2:2′-disulphonic acid instead of the radical of benzidinemonosulphonic acid. Thus the animo-monoazo compound—



is diazotised and coupled with 2-ethoxy-1-naphthylamine-6-sulphonic acid, and the resulting aminodisazo compound is diazotised and coupled with 1-acetylamino-8-naphthol-4-sulphonic acid in presence of pyridine. The product is converted to the copper complex by heating at 98–100°c. with $CuSO_4$ in presence of aq. sodium acetate and acetic acid. E. S.

Pechmann Dye. American Cyanamid Co. *USP* 2,640,836

The so-called red "Pechmann dye" of possible formula—



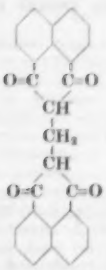
is prepared in yields of up to 80% by carrying out the original reaction of heating β-benzoyl-acrylic acid in acetic anhydride, in the presence of copper or a copper salt and an acid of boron. Thus, all parts being by weight, β-benzoyl-acrylic acid (50), cuprous chloride (10) and boric acid (36) are refluxed in acetic anhydride (33). β-Benzoyl-lactic acid may replace the corresponding acrylic acid derivative.

USP 2,640,837

An ammonium salt of a mineral acid replaces the boric acid. R. K. F.

Perinaphthindan-1:3-dione Derivatives—Pigments. Basf. *BP* 712,166

Perinaphthindan-1:3-dione and its 2-Alk derivatives which may also be substituted in the other part of the mol. are treated with a non-aromatic aldehyde to give yellow pigments suitable for colouring paper or spin-dyeing. Thus the pigment—



is made by running 30% aq. formaldehyde into a boiling solution of perinaphthindan-1:3-dione in 85% formic acid. R. K. F.

Phthaloylacylaminocarbazole Acid Dyes. FBy. *BP* 711,640

1-Acylamino-4-(*p*-phenylanilido)anthraquinones are cyclised to the corresponding carbazoles, and if not already containing a SO_3H, are sulphonated to produce brown wool dyes. Thus 1-benzoylamino-4-(*p*-phenylanilido)anthraquinone is treated with H_2SO_4 at 30°C. for 2 hr., 20% oleum added and treatment continued until a test is soluble in water. Nitrosyl sulphuric acid is added and the dye separated by pouring into water. R. K. F.

Onium Salts of Dibenzanthrones. General Aniline. *USP* 2,619,492

Halogenomethylated derivatives of dibenzanthronyls, dibenzanthrones and *iso*dibenzanthrones are treated with a tertiary amine, e.g. pyridine, to form soluble quaternary salts; or with a thiourea, e.g. tetramethylthiourea, to form soluble thiouronium derivatives. Thus dichloromethyldibenzanthrone, and 1:1:3-trimethylthiourea are heated in water under reflux for 30 min. The product, suitable for the direct printing of cotton, is separated by diluting with acetone. R. K. F.

Tetra-Aza-Porphins—Pigments. R. P. Linstead, M. Whalley, and G. E. Ficken. *BP* 713,208

A method, specially suited for preparing magnesium tetra-azo-porphins containing < 3 aromatic or quinonoid rings fused on to the pyrrole nuclei, is to treat a maleic dinitrile, a Δ'-tetrahydrophthalonitrile, a phthalonitrile, or a heterocyclic *o*-dinitrile, or mixtures thereof, with a magnesium alcoholate, or the compound obtained by decomposing a Grignard reagent with an alcohol. Thus a suspension of magnesium *n*-propoxide, prepared by heating magnesium with *n*-propanol, is refluxed with maleic nitrile for 20 min. After removing the *n*-propanol under reduced pressure, the pigment magnesium tetra-azo-porphin is extracted from the residue with boiling benzene containing a trace of methanol. R. K. F.

Alkali Metal Phthalocyanines. Ciba. *BP* 712,455

Alkali metal phthalocyanines are made by treating a solution of phthalonitrile in an alcohol of b.p. > 130°C., with a suspension of an alkali metal hydride in an inert organic solvent, e.g. a hydrocarbon. Thus sodium hydride suspended in xylene is added in small portions to phthalonitrile in a mixture of amyl alcohol and xylene at 95°C., followed by refluxing for 3 hr. R. K. F.

Phthalocyanine Pigments. American Cyanamid Co. *BP* 712,378

Metallised phthalocyanines are converted to tinctorially strong forms by grinding in presence of an organic liquid and a solid grinding aid having a surface area of 0·14 to 1·38 sq.m. per g. Thus, all parts being by weight, acid-pasted copper phthalocyanine (605), aniline (1,210) and microatomised salt (5,460) having a surface area of 0·14 sq.m/g. are mixed for 12 hr. below 30°C. in a dough mixer. Separation is effected by slurrying in dil. HCl.

BP 712,379

Halogen-free metallised phthalocyanines are converted to tinctorially strong forms by kneading in a dough mixer with a finely ground solid grinding aid and 1·5 to 2 times the weight of phthalocyanine, of an aromatic or aliphatic amine, a monohydric phenol, or pyridine, or furfural.

BP 712,380

Following the synthesis of a phthalocyanine in presence of an organic solvent, a finely ground grinding aid is introduced and the mixture ground to produce a tinctorially strong pigment, without further processing. Thus after preparing copper phthalocyanine from phthalonitrile, NH_3 and $CuSO_4$ in nitrobenzene; the mixture is cooled, micropulverised salt added and the Eppenbach stirrer speeded from 2,000 r.p.m. to 5,000 r.p.m. until the desired pigment particle size is obtained. R. K. F.

Phthalocyanines, Acid Pasting of. General Aniline. *BP* 711,677

Phthalocyanines are acid-pasted to make them suitable for use as pigments by treating with the just sufficient acid, e.g. H_2SO_4, of concn. 68–100% to produce a kneadable mass, which is then subjected to a uniform shearing action, such as that obtained in a Werner-Pfleiderer mill. Thus, all parts being by weight, copper hexadecachlorophthalocyanine (100) and 96% H_2SO_4(300) are milled in a Werner-Pfleiderer mill for 15 min. Separation is effected by diluting with water (3500). R. K. F.

Phthalocyanine Pigments. DuP. *USP* 2,645,643

In the grinding of phthalocyanines in presence of e.g. salt (cf. *USP* 2,402,167) and a water-immiscible liquid (cf. *USP* 2,556,728 and 2,556,730: J.S.D.C., **68**, 191, 192 (1952)) a small amount of a polytitanium or sorbitan ester of a long-chain fatty acid is added to give pigments of improved texture and tinctorial properties. Thus, chlorine-free phthalocyanine (3 lb.), salt (27 lb.) and a solution of polytitanium stearate (1 oz.) in trichloroethylene (13 oz.) were milled together in a steel ball mill. The resulting mixture was then steam-distilled, filtered and treated with aq. HCl. R. K. F.

Cyanine Dye Salts. DuP. *USP* 2,647,116

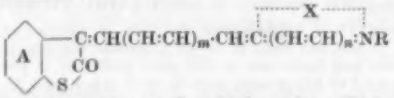
Mono- and tri-methincyanine dyes having a *n*-butanesulphonate anion and a methyl or ethyl group attached to the heterocyclic N atom have good solubility in water and do not leave residual stain in finished photographic elements. C. O. C.

Cyanine Dyes. DuP. *USP* 2,647,115

The lower alkyl esters of *cyclo*hexanemonosulphonic acid and its monoalkyl (3–4 C) substituents react readily and smoothly with heterocyclic bases containing a reactive methyl group in the α- or γ-position to the heterocyclic N atom to form quaternary or *cyclo*ammonium salts. These salts can be readily converted into cyanine dyes by various condensation reactions, e.g. by condensation with an ortho ester of a monocarboxylic acid in presence of an acid binding agent. C. O. C.

***mero*Cyanine Dyes.** R. H. Glauert and F. G. Mann. *BP* 712,651

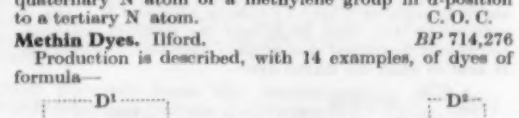
Dyes of formula—



(n = 0 or 1; m = 1 or 2; R = hydrocarbon; X = atoms to complete a 5- or 6-membered ring or a polycyclic homologue thereof; the benzene nucleus A may be substituted or carry a fused-on ring) are obtained by heating a suitable thio-oxindole with the product of reacting together a dianil of malondialdehyde or glutacondialdehyde which may contain hydrocarbon substituents and a quaternary salt of a heterocyclic N compound carrying a CH_3 or C_2H_5 group in α- or γ-position to the quaternary N atom or a methylene group in α-position to a tertiary N atom. C. O. C.

Methin Dyes. Ilford. *BP* 714,276

Production is described, with 14 examples, of dyes of formula—



(R^1 and R^3 = Alk, aralkyl or hydroxyalkyl; R^2 = Alk, Ar or aralkyl; R^4 = H, Alk, Ar or aralkyl; a and b = 0 or 1; X = O or S; D^1 and D^2 = atoms to complete 5- or 6-membered rings). C. O. C.

Methin Dyes. Kodak. *BP* 713,255
BP 713,293

Methin dyes containing a group of formula—

(Z = atoms to complete a dihydropyrrole nucleus, a pyrrole nucleus carrying a fused-on ring or a trihydropyridine or a 5:6-benz-3-thiazine nucleus are photographic sensitisers. 55 examples are given. C. O. C.

Acid Dyes of Very Good Fastness. FH. *BP* 712,037

Acid dyes containing one or more SO_2-CR:CH_2 (R = H, low mol. wt. hydrocarbon or Br) groups yield dyeings or prints of very good fastness properties. The dyes may belong to any chemical class. C. O. C.

Non-dusting Water-insoluble Rayon Dyes. ICI *BP* 713,541

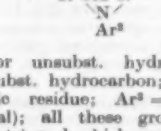
The dry powdered dye is mixed with 0·5–5·0% by wt. of the condensate of 1 mol. of an organic hydroxy compound with < 2 mol. of ethylene oxide, e.g. the condensate of 1 mol. octylcresol and 10 mol. of ethylene oxide. C. O. C.

Pigments from Coloured Polyvinyl Chloride. Basf. *BP* 712,219

Atomised polymers or copolymers of vinyl chloride are very voluminous and have a particularly soft and fine grain. It can be dyed with basic dyes e.g. *C.I.* 655, 662, 729, 741, 786, 788, 797, 841 or 922 or Astraphloxin FF extra (*BP* 232,740: cf. J.S.D.C., **41**, 335 (1925)) to yield pigments which may be used directly. They are readily pasted with binding and thickening agents, etc. to yield inks or paints which give prints or coatings of good, and in some cases surprisingly good, fastness to light. Use of fluorescent dyes, e.g. *C.I.* 749, 750, 753, 815 or amino-1:8-naphthalimide (*BP* 352,139) gives pigments which fluoresce in daylight or in ultraviolet radiation. C. O. C.

Fluorescent Brightening Agent. Ilford. *BP* 712,764

Compounds of formula—



(R^1 = subst. or unsubst. hydrocarbon; R^2 = H or subst. or nonsubst. hydrocarbon; Ar^1 = subst. or nonsubst. aromatic residue; Ar^2 = subst. or nonsubst. aromatic radical); all these groups being free from nitro substituents) and which are colourless in aqueous or alcoholic solution, have strong bluish fluorescence in daylight and slightly less fluorescence in artificial light. They have good fastness to light. C. O. C.

Metallic Powders. Glacier Metal Co. *BP* 712,699.

Metal powders, particularly of copper or its alloys, are prepared by atomising a jet of molten metal by use of a liquid or gaseous inert agent, e.g. N_2 or solid CO_2 in alcohol, in presence of H resulting either from addition of H or a H-forming substance with the molten metal in the crucible and/or supplied to an enclosed zone between the discharge nozzle for the molten metal and the atomising nozzle. This avoids any oxidation in the atomising zone.
BP 713,009

Molten metal atomised by an inert gas is chilled to below its freezing point by a freely dispersed spray or mist, the whole of the cooling liquid being evaporated so that it can be carried away by the atomising gas. C. O. C.

Chalking of Titanium Dioxide. Its Evaluation by the Mandelic Acid Paste Method (V this page).
Problems of Dyes for Synthetic Fibres (VIII p. 471).
Dyeing Polyamides and Polyurethans with Nitroso Dyes (VIII p. 472).
Cerium (IV) Sulphate Oxidation of Phenols (XIV p. 478).

V— PAINTS; ENAMELS; INKS

Chalking of Titanium Dioxide. Its Evaluation by the Mandelic Acid Paste Method. S. Todicco. *Ind. Vernice* (Milan), **8**, 17–20 (1954); *Chem. Abs.*, **48**, 7316 (25 June 1954).

That light catalyses reduction of TiO_2 to Ti_2O_3 with simultaneous oxidation of the vehicle, air then regenerating the TiO_2 leaving the vehicle oxidised, is shown by grinding TiO_2 in glycerol in presence of mandelic acid with resulting formation of C_6H_5OH. This procedure is adopted to a control method by exposing ground pigment in shallow Plexiglas dishes covered with thin (0·2 mm.) cover glasses and sealed with Plexiglas in acetone. A considerable number of such dishes are placed closely to and under a tubular ultraviolet source of 300–600 mμ. (maximum emission at 400 mμ.). The change is followed by observing changes in reflectance (green filters) of the samples and plotting reflectance against log of exposure time. The method is not very sensitive but enables ready recognition of highly chalking and non-chalking pigments. C. O. C.

PATENTS

Cellulose Nitrate Lacquers, etc. ICI. *BP* 713,189

When liquid trialkylpentaerythritol ether ethyl carbonate is added to cellulose nitrate dissolved in a volatile organic solvent compatible with the ester, a solution results which will yield clear tack-free films. On subjecting these films to conditions which polymerise the ester, e.g. by heating or preferably by air oxidation in presence of a drier, they remain clear and non-tacky. C. O. C.

Non-smudging Ink for Carbon or other Transfer Papers. Ontario Research Foundation. *USP* 2,647,060

A dispersion in an organic solvent of a wax–oil–dye blend, a friable resin (as hardening agent), a primary amide of a long chain fatty acid (as thickening agent), a film forming agent and a filler, gives a duplicating ink for application to carbon papers, etc. which is non-smudging yet can be broken by the pressure of a pencil and has excellent transfer properties undiminished by ageing. C. O. C.

Aqueous Pigment Pastes. Monsanto. *USP* 2,647,094

Aqueous pigment pastes having dispersant properties, i.e. which can be used to disperse film-forming materials by mild agitation in water, are produced by forming a water-insoluble styrene-maleic ester copolymer and a water-insoluble pigment into an aqueous slurry and then adding ammonia or a volatile amine. C. O. C.

Polymethacrylate Ester Coatings. DuP. *BP* 709,952

Polymethacrylate esters of alcohols or glycols of < 5C atoms are degraded in mol. wt. by severe mechanical milling and then give solutions which can be sprayed without "webbing" defects. E. C.

Insecticidal Surface Coatings. National Research Development Corpn. *BP* 709,721

An insecticide, e.g. benzene hexachloride, dichlorodiphenyltrichloroethane, etc., is incorporated in a solution of a butanol-modified urea- or melamine-formaldehyde resin plasticised with an alkyd resin, in amount sufficient to cause blooming from the dry cured resin, and a cold-curing catalyst, e.g. sulphuric acid, is added immediately before application of the solution as a surface coating. E. C.

Pigments from Coloured Polyvinyl Chloride (IV this page).

VI— FIBRES; YARNS; FABRICS

Review of Textile Research and Development during 1953. R. Steele, C. Messler, and R. K. Towers. *Text. Research J.*, **24**, 438–490 (May 1954).

A bibliography containing 1887 references is given. A. B.

Literature Survey on Fibre Friction. J. H. Langston and W. T. Rainey. *Text. Research J.*, **24**, 643–653 (July 1954).

Abrasion Damage of Textile Fibres. G. Susich. *Text. Research J.*, **24**, 210–228 (March 1954).

The inherent abrasion behaviour of 14 different textile materials in the form of yarns has been investigated. Abrasion damage was measured quantitatively by the fibre fineness destroyed in flexing around a steel bar using

the Stoll–Quartermaster abrasion tester. The damage of multifilaments increases from nylon to Dacron polyester fibre, viscose rayon, Fortisan, Orlon acrylic fibre, Saran, silk, acetate rayon and casein, while that of staple yarns increases from nylon to Dacron, cotton, Fibravyl, dynel, Kwalon, Thermovyl, wool, Orlon, viscose rayon, and acetate rayon. A. B.

Occurrence, Behaviour, and Elimination of Static on Textiles. R. D. Fine. *Amer. Dyestuff Rep.*, **43**, P 405–P 408 (21 June 1954).

Static Problems affecting Knitting. C. H. Edwards. *J. Textile Inst.*, **45**, P 248–P 257 (June 1954).

Capacity, Dielectric Constant, and Power Factor of Fibre Assemblies. J. W. S. Hearle. *Text. Research J.*, **24**, 307–321 (April 1954).

Measurements of the effective dielectric constant and the power factor of yarns wound between two cones have been made for a number of materials at various densities of packing, at frequencies between 50 c./sec. and 200 kc./sec., and under different moisture conditions. The results are used to check the relation between electrical resistance and dielectric constant, and are discussed in their relation to the structure of the material. A. B.

Improvement of Lustre of Cotton. VII—Fibre Properties and Variety Characteristics in relation to Lustre. L. Fourt, R. M. Howarth, N. B. Rutherford, and P. Streicher. *Text. Research J.*, **24**, 279–291 (March 1954).

The entire range of American cotton production has been examined for correlation of lustre with other fibre properties over two crop years. Lustre is shown to be a varietal characteristic, although influenced also by environmental factors. The strongest correlations are of higher lustre with greater length, greater strength, and greater roundness. A. B.

Improvement of Lustre of Cotton. VIII—Selection within Commercial Varieties on the Basis of Fibre Properties. L. Fourt, R. M. Howarth, M. B. Rutherford, and P. Streicher. *Text. Research J.*, **24**, 685–694 (July 1954).

Factors affecting the Tear- and Water-resistance of Lightweight Clothing and Tentage Fabrics. W. E. O'Brien and L. I. Weiner. *Text. Research J.*, **24**, 241–250 (March 1954).

Strength and water-resistance data are given for a series of light-weight cotton fabrics varying in weave, weft yarn type, weft cover factor, and finish. The results indicate that the sateen has better tear strength than the wind-resistant twill, but poorer water-resistance characteristics. The tighter weaves are less penetrable but more easily torn. Mercerisation improves the tear strength but lowers the water-resistance. A. B.

Optical and Electron Microscopic Studies of Cotton Fibre Structure. M. L. Rollins and V. W. Tripp. *Text. Research J.*, **24**, 345–357 (April 1954).

The appearance, growth, and structure of a cotton fibre are described, and photomicrographs and electron micrographs are used to illustrate both gross and fine features of the cell wall morphology. Methods have been developed during this study for isolation of individual components of the cell wall for purposes of electron microscopy. Details of the structure of the primary wall and the winding layer are described. A. B.

Degradation of Cotton Fibres and Yarns by Heat and Moisture. R. S. Orr, L. C. Weiss, G. C. Humphreys, T. Mares, and J. N. Grant. *Text. Research J.*, **24**, 399–406 (May 1954).

Strength and elongation measurements have been made on single cotton fibres and on yarns which have been subjected to various temperatures from 110° to 162°c. and various moisture conditions from 3% R.H. up to saturation for periods of heating from 2 to 128 hr. Moisture contents and degrees of polymerisation were also determined. An equation relating fibre strength loss to time of heating and percentage of cellulose links broken is discussed. A. B.

Distribution of "Cellulose" and "Hemicellulose" in the Cell Wall of Spruce, Birch, and Cotton. S. Asunmaa and P. W. Lange. *Svensk Papperstidning*, **57**, 501–516 (31 July 1954).

The distribution of material in various fibres derived from spruce and birch holocellulose and cotton, and esterified with *p*-phenylazobenzoyl chloride, was measured microspectrographically. In cotton "cellulose" is fairly evenly distributed across the cell wall, and a small amount of "accessible" material is deposited mainly in the outer regions of the fibre wall. S. V. S.

Microscopy in Cellulose Research. M. L. Rollins. *Anal. Chem.*, **26**, 718–724 (April 1954).

The present picture of fibre morphology, though still incomplete, has resulted largely from the application of light microscopy, assisted by staining and swelling techniques and observations of birefringence. Phase-contrast microscopy (which eliminates the need for staining), the use of polarised light, and ultraviolet and infrared irradiation are new techniques which have as yet hardly been applied to cellulose studies. The scope of these latter methods is briefly discussed. Electron microscopy, though capable of much higher magnifications than are obtainable with light methods, is of limited value, since extremely thin sections are essential (cellulose absorbs electrons strongly); this has, however, led to useful advances in manipulative and microscopical techniques. The development of methods (such as that of beating in water in a Waring Blender) for isolating individual cell wall components for electron-microscopical work has permitted also interesting observations with the light microscope. Studies are reviewed, and illustrated by reproductions of photo- and electron-micrographs, which throw light on the structure and the composition of the primary wall, and illustrate its restrictive action (also indicated by quant. measurements of shrinkage in the isolated primary wall) on fibre swelling. In certain substitution reactions the secondary wall of the fibre is greatly swollen, thus placing the intermediate "winding layer" under considerable tension; this has been stated (W. A. Sisson) to bring about resistance to intramicellar swelling, and may thus account for the apparent lack of reactivity and the lower degree of substitution of the "winding layer" cellulose. J. W. D.

Structures of Native and Mercerised Celluloses. J. O. Warwicker; H. J. Wellard; and H. J. Woods. *Nature*, **174**, 135–136 (17 July 1954).

Warwicker and Wellard comment separately upon the report of Sen and Roy (*Nature*, **174**, 298 (13 Feb. 1954)) that they had observed new equatorial reflexions in the X-ray diagrams of native and mercerised celluloses, the corresponding mean spacings being 13·6 A. and 14·4 A. respectively. Warwicker considers that the observed reflexions may be spurious, and possibly due to the diffraction of certain components of the "white" radiation present in an X-ray beam when filtered or unfiltered radiation is used. The work of Sisson, Clark, and Parker (*J. Amer. Chem. Soc.*, **58**, 1635 (1936)) is instanced. Wellard maintains that a reflexion at $2\theta \simeq 6°$ probably results from Kα radiation from the Cu anode of the tube (this would correspond to a spacing of ~ 14 A.); he comments also that the two strong planes (002) and (101) of Cellulose II are not resolved at $2\theta \simeq 6°$ in X-ray cameras normally used for fibre work, the extra reflexion thus appearing single, and that similar reflexions are produced, under the same tube conditions, from other substances, e.g. graphite. Woods disagrees with the views of Warwicker and Wellard, and claims that the reflexion in question has long been observed with jute under conditions which are at variance with those required by their hypotheses; he differs from Sen and Roy, however, in holding that the reflexion does not occur in ramie photographs taken under the same conditions. There is evidence, as yet inconclusive, that degradation of ramie fibres may, under certain circumstances, lead to the appearance of this reflexion or one of similar spacing. J. W. D.

Hydrolysis of Cellulose. II—Acid-sensitive Linkages in Egyptian Cotton. A. Sharples. *J. Polymer Science*, **14**, 45–104 (July 1954).

Hydrolytic study of the kinetics of chain degradation can be used to detect presence of acid-labile linkages in cellulose, if the amount of ordered or crystalline material

is first reduced by treatment involving regeneration from alkaline solutions. Results from Egyptian cotton regenerated from benzyltrimethylammonium hydroxide in absence of oxygen show that less than one acid-labile linkage per 2900 glucose residues can be present in the original chain molecules. It is possible that even this small amount is produced during the alkali treatment. Thus weak bonds of the types suggested by Schulz and Pacsu are definitely absent. Cotton regenerated from cuprammonium and cupriethylenediamine solutions, however, does contain randomly distributed linkages which are approx. 10,000 times more sensitive to acids than the normal glycosidic type. They appear to be formed from a limited number of special sites in the chain molecules, by oxidation in alkaline solution. Assuming the value of P_n for undergraded cotton to be 2900, there is one of these extranormal linkages per 660 glucose residues. C. O. C.

Swelling Powers of Urea Solutions on Cellulose. J. M. Preston, J. F. Clark, W. R. Beath, and M. V. Nimkar. *J. Textile Inst.*, **45**, T504–T509 (July 1954).

The behaviour of cellulose fibres in urea solutions is studied, using centrifuge swelling measurements, direct transverse swelling measurement, and loss in strength on extension. The action is more marked than water, and the increase is approximately proportional to the concentration, and can amount to 30% or more. It is probably due to bond breaking between contiguous cellulose molecules, including those which are normally tightly bonded together even when swollen in water. This may result from preferential urea–cellulose hydrogen bonding, perhaps assisted by the high dielectric constant of the urea solution. Dye stripping is more rapid in solutions of urea. J. W. B.

Preparation and Properties of some Inorganic Alginate Fibres. M. J. Dudgeon, R. S. Thomas, and F. N. Woodward. *J.S.D.C.*, **70**, 230–237 (June 1954).

Alginate fibres have been produced in which alginic acid is combined partly with calcium and partly with other metals. In the case of all the metals examined (chromium, copper, cadmium, tin, bismuth, barium, zinc, and aluminium) there is a reduction in water imbibition, but, with the exception of aluminium, barium, and cadmium, this is accompanied by a reduction in dry and wet extensibilities. Calcium–cadmium alginate appears to be most promising, since, compared with calcium alginate fibre, it shows no loss in dry extensibility, an increased wet tenacity, and only a small loss in dry tenacity, and, moreover, can be produced with no more difficulty than calcium alginate. AUTHORS

Morphological and Chemical Examination of Wool —I and II. H. Zahn. *Textil-Praxis*, **9**, 515–521 (June); 663–667 (July 1954).

A lengthy and well illustrated review with 29 references. The structural elements of the fibre are considered in turn, and the chemistry of wool protein is examined. The preparation of rot-proofed wool by chemical modification is dealt with in some detail, in particular a treatment with 4:6-bischloromethyl-1:3-dimethylbenzene. S. R. C.

Terminal Carboxyl Groups in Wool Keratin. S. Blackburn and G. R. Lee. *J. Textile Inst.*, **45**, T487–T488 (June 1954).

Wool is heated with anhydrous hydrazine, when all the amino-acid residues are converted to hydrazides except the terminal ones which carry free α-carboxyl groups. After removal of excess hydrazine the residue is dissolved in water and applied to a carboxylic ion-exchange column, which retains the hydrazides and allows only the free amino acids to pass. Paper chromatograms of the eluate give spots of equal intensity due to glycine, alanine, serine, and threonine, which, on the assumption that degradation of the chain prior to hydrazide formation did not occur, are therefore presumed to constitute the terminal α-carboxyl groups in wool. They are fewer in number than the terminal α-amino groups, and the results are also consistent with previous evidence that the peptide chains are fairly long. J. W. B.

Bilateral Asymmetry of Melanin Distribution in Pigmented Wools and its Correlation with Fibre Crimp. G. Laxer, C. S. Whewell, and H. J. Woods. *J. Textile Inst.*, **45**, T482–T486 (June 1954).

Crimped pigmented wool fibres are relaxed and examined under the microscope, when it is seen that pigmentation is asymmetrically distributed, being heavier in the side of the inner curvature. The phenomenon is not readily observable in pigmented keratin fibres of relatively long wavelengths. Clearer definition is obtained by partial bleaching with a ferrous ion–peroxide system; thick cross-sections then show that oval fibres are more heavily pigmented on one side of the major axis. This portion is also more resistant to tryptic digestion. J. W. B.

Diffusion-controlled Sorption of Water by Wool Fibres. N. F. Roberts and A. R. Haly. *Text. Research J.*, **24**, 261–262 (March 1954).

Attempts have been made to measure the rate at which the regain of a wool fibre comes into equilibrium with the atmosphere at its surface when diffusion is the only rate-controlling process. The regain changes take several times as long as would be expected from previous data on the diffusion of water in horn keratin. A. B.

Selective Absorption of Optical Antipodes by Proteins. W. Bradley and R. A. Brindley. *Chem. and Ind.*, 579–580 (15 May 1954).

When wool is first combined with *p*-methoxymandelic acid and then immersed in water, a portion of the acid passes into the medium, leaving combined a fraction which is enriched in respect of the dextrorotatory component. J. W. B.

Effect of *o*-Chlorophenol on Wool. H. M. Appleyard and C. M. Dymoke. *J. Textile Inst.*, **45**, T480–T482 (June 1954).

When cross-sections of Lincoln wool fibres are mounted in *o*-chlorophenol, cell boundaries gradually become clear, and an excellent photograph can be taken, using phase-contrast. The full network can be seen only for a very short time and soon disappears; this may be due to the dissolution of protein material, perhaps from the cortical cell boundaries. J. W. B.

Thermal and Elastic Properties of α-Keratin. H. B. Bull. *J. Phys. Chem.* **58**, 101–3 (1954): *Chem. Abs.*, **48**, 7085 (25 June 1954).

When the coefficient of elasticity of human hair was measured at 25 and 85°c. two maxima were observed. The first, at 5% extension, was not sensitive to temperature or the previous heating of the hair whereas the second, at ca. 40% extension at 25°c., was sensitive to both. The volume of the fibre was minimum at ca. 5% and maximum at ca. 30% stretch. There were conspicuous and sharp maxima in the energies of activation for the decay of the stress of a hair fibre at ca. 5% and ca. 20% stretch. Typical protein denaturants have no large effects on the elastic properties of hair; this indicates that hydrogen bonds are not primarily responsible for the elastic properties of hair. Emphasis is placed on the disulphide bonds. Whatever molecular folding of the peptide chains may have been originally present in the hair follicle has been extensively deformed by formation of interchain disulphide bonds. C. O. C.

Relaxation of Stretched Animal Fibres. II— Relaxation of Human Hair. G. C. Wood. *J. Textile Inst.*, **45**, T462–T471 (June 1954).

Relaxation curves of human hair stretched 10–50% in aqueous media are determined, using an instrument which enables measurements to be made during the first few hundredths of a second. Results are obtained for untreated hair and hair modified by treatments known to rupture the disulphide bonds, and the effect of relaxing in hydrochloric, thioglycollic, and formic acid is studied. It is shown that, following the initial stretch, there is a rapid fall of tension, probably due to breakage of hydrogen bonds and consequent rearrangement of long-chain molecules. A slower relaxation, complete only after many hours, is due to fission, probably hydrolytic, of the disulphide bonds. J. W. B.

Molecular Size, Shape, and Aggregation of Soluble Feather Keratin. A. M. Woodin. *Biochem. J.*, **57**, 99–109 (May 1954).

The preparation of solutions of feather keratin by dispersion in urea and bisulphite and by oxidation with performic acid is described. The cysteine : cystine ratio of keratin dissolved in solutions of urea and bisulphite depends on the urea concentration and on the pH. The physical properties of keratin in solution have been measured and correlated with the cystine and cysteine contents. Measurements of osmotic pressure, turbidity, sedimentation rate, and viscosity indicate that in infinitely dilute solution keratin has a mol. wt. of 10,000 and an axial ratio of 13.

Preparations which contain both free thiol groups and disulphide bonds associate with increasing concentration. It is concluded that the association involves the formation of intermolecular disulphide bonds at the expense of intramolecular bonds. Association produces a particle which is more asymmetric than the monomer.

Keratin sediments with a single boundary in the ultracentrifuge. The variation of the viscosity, osmotic pressure, sedimentation rate, and turbidity with concentration of dissolved keratin is discussed. P. G. M.

Silk–Phosphoric Acid Solutions. J. Schurz. *Nature*, **173**, 952–953 (15 May 1954).

Ultraviolet spectrograms are obtained for (1) natural silk, (2) solutions of silk in phosphoric acid, (3) aqueous solutions of silk obtained by dialysing (2), and (4) silk films obtained by drying (3). On the assumption that intermolecular hydrogen bonding is shown by a specific absorption at 250 mμ. the results indicate that natural silk contains most intermolecular bonds, which decrease in the order (1) > (4) > (3) > (2), the phosphoric acid solution having lost nearly all of them. Further observations are made on the question of molecular decomposition by various silk solvents. J. W. B.

Complementary Nature of Fibres from Natural and from Synthetic Polymers. J. B. Quig and R. W. Dennison. *Text. Research J.*, **24**, 361–373 (April 1954).

Detailed investigations of the properties of fabric blends have led to the conclusion that fibres from synthetic and from natural polymers are complementary in nature. Among the fabric characteristics examined were strength, abrasion resistance, recovery from wrinkling, ability to retain a pressed crease, flammability and the sensitivity of certain of these properties to humidity, dry cleaning, and laundering. The fibres used were nylon, Dacron polyester staple, or Orlon acrylic staple combined with rayon staple, acetate staple, or wool. A. B.

Macromolecular Chemistry and Synthetic Fibres. H. Staudinger. *Melliand Textilber.*, **35**, 719–720 (July 1954).

An address of general interest. S. R. C.

Nylon-type Oligamides. C. D. Cowell. *Chem. and Ind.*, 577 (15 May 1954).

The following oligamides of polymethylene adipamide corresponding to 66-nylon have been synthesised—

(I)

$R{\cdot}CO{\cdot}[CH_2]_x{\cdot}CO{\cdot}NH{\cdot}[CH_2]_y{\cdot}NH{\cdot}CO{\cdot}[CH_2]_x{\cdot}CO{\cdot}R$

where

(*A*)	$x = 4$	$y = 6$	R = $O{\cdot}CH_3$, OH, $NH{\cdot}[CH_2]_3{\cdot}CH_3$
(*B*)	$x = 8$	$y = 6$	R = $O{\cdot}CH_3$, OH
(*C*)	$x = 4$	$y = 10$	R = $O{\cdot}CH_3$, OH

(II)

$R{\cdot}NH{\cdot}[CH_2]_6{\cdot}NH{\cdot}CO{\cdot}[CH_2]_x{\cdot}CO{\cdot}NH{\cdot}[CH_2]_6{\cdot}NH{\cdot}R$

where

(*A*)	$x = 4$	R = H, $CO{\cdot}CH_3$
(*B*)	$x = 8$	R = H
(*C*)	$x = 4$	R = $-CO{\cdot}[CH_2]_4{\cdot}CO{\cdot}R'$ (R' = OH, $O{\cdot}CH_3$)
(*D*)	$x = 8$	R = $-CO{\cdot}[CH_2]_6{\cdot}CO{\cdot}R'$ (R' = OH, $O{\cdot}CH_3$)

J. W. B.

Influence of Heat and Swelling Agents on 66-Nylon Yarns. I— General Experiments on Length Equilibria. M. V. Forward and H. J. Palmer; **II— Changes in Length with Time in Aqueous Swelling Media.** H. J. Palmer; **III— Changes in Length at Equilibrium in Dilute Non-aqueous Phenol Solutions.** M. V. Forward. *J. Textile Inst.*, **45**, T510–T538; T539–T558; T559–T568 (July 1954).

I— Equilibrium length changes of drawn and undrawn 66-nylon on heating and on immersion in swelling agents are studied. Both cause reversible and irreversible changes. The reversible change on heating is caused by an increase in entropy; the length of drawn and undrawn yarn decreases and increases respectively. The reversible increase due to swelling agents is a reflection of the volume increase caused by uptake of reagent. Irreversible changes are probably caused by rupture of interchain bonds followed by rearrangement of molecules associated with them. The mechanism of heat setting is largely the same as that of the action of a swelling agent, increasing severity leading to further inter-chain bond rupture and greater irreversible length change.

The distribution of phenol between water and nylon is investigated at different concentrations and temperatures and with yarns annealed under various conditions.

II— Changes in length with time of 66-nylon yarns in water and aqueous phenol solutions are examined using conditioned relaxed samples, and swollen and reconditioned samples, of yarns of different denier and different degrees of molecular orientation. On immersion, there is an imbibition period during which the unpenetrated core holds the yarn at its original length, resulting in some transverse orientation in the outer swollen layers. If the imbibition period is long, there is an approach to equilibrium in the transverse orientation, and ensuing changes in length are small. As the imbibition period is directly related to filament denier, the rate and the magnitude of the change are inverse functions of denier. Wetting the yarn prior to immersion virtually removes the imbibition period and increases the equilibrium length change. The processes are interpreted in terms of the rupture of interchain bonds up to a certain energy level, thus giving a network of unpenetrated and penetrated regions. In the latter, the more mobile molecules re-form and develop new interchain bonds, giving a set structure which assists in controlling length changes.

III— Drawn and undrawn nylon is swollen in various organic liquids and in 1% solutions of phenol in the organic liquids. Some, e.g. ethanol, chloroform, are good swelling agents; others, e.g. benzene, *cyclo*hexane, have no action. The swelling power is to some extent, though with anomalies, related to the polar nature of the liquid. Correlation with known physical constants of the liquids is very poor and supplies no information on the reaction with nylon. The solvent has a large effect on the swelling of yarn in phenol solutions, and correlation of swelling power with the frequency shift of OH vibrations in infrared spectra is good. Three types of swelling behaviour are distinguished, and organic solvents are classified on that basis. J. W. B.

Infrared Dichroism of Nylon and Polyethylene Terephthalate. R. G. Quynn and R. Steele. *Nature*, **173**, 1240 (26 June 1954).

Four nylon absorption bands show parallel dichroism at lower draw ratios, changing over to perpendicular dichroism as drawing proceeds. Similar results are obtained with polyethylene terephthalate. X-Ray patterns or birefringence measurements gave no evidence of a major reversal of chain orientation as implied by the infrared results. Measurements of infrared dichroism of fibres may reveal chain orientation not detected by the usual X-ray and optical techniques. It is possible that in poorly oriented fibres the amorphous regions have a chain orientation quite different from that attained in fully drawn crystalline material, and that at lower extensions the orientation of the amorphous regions largely determines the infrared dichroism. W. R. M.

Infrared Spectrum of Terylene. G. J. Weston. *Chem. and Ind.*, 604 (22 May 1954).

The infrared spectrum of unoriented Terylene over the range 2·5–4·0 μ. has been studied using a prism of LiF.

There are bands at ~3·5μ. corresponding to C–H stretching modes, and a sharp peak at 2·91μ. which may be due to OH chain-ending groups in the mol. Using polarised radiation and oriented film at 90° to the beam direction, the following bands have been observed— (*a*) at 3080 cm.$^{-1}$, showing little or no dichroism; (*b*) at 2980 cm.$^{-1}$ and 2920 cm.$^{-1}$, both showing parallel dichroism— the former is very unsymmetrical and has an underlying component with a peak at ~ 3020 cm.$^{-1}$ which exhibits perpendicular dichroism; (*c*) at 2850 cm.$^{-1}$, showing perpendicular dichroism. The assignment of these peaks to specific C–H stretching modes is not yet definite; the possibilities are discussed. Certain of the observations appear to disagree with the findings of Miller and Willis (*Trans. Faraday Soc.*, **49**, 433 (1953)), as do also the observations that the spectrum of oriented Terylene in the 7μ. region shows a peak at 1465 cm.$^{-1}$ which shows parallel dichroism, and an overlapping band at 1480 cm.$^{-1}$ exhibiting perpendicular dichroism. In an added note, Miller and Willis consider that the peak at 2·91μ. is more probably the first overtone of the CO stretching frequency at 1725 cm.$^{-1}$.

J. W. D.

Acrylic Fibres. III— Copolymerisation of Acrylonitrile and Acrylamide. H. Reichert. *Faserforsch. und Textiltech.*, **5**, 204–210 (May 1954).

An exposition of the theory of the kinetics of copolymerisation is given. A 6% aq. soln. of acrylonitrile, acrylamide, or a mixture of these monomers is caused to react under the free-radical polymerisation conditions previously described (see J.S.D.C., **70**, 317 (July 1954)), the (co)polymer obtained being isolated by coagulation with methanol or aq. NaCl (high-amide products, which are formed as clear solutions or colloidal systems), or by simple filtration (high-nitrile products). Analysis of the copolymers obtained shows that their amide : nitrile ratios are always greater than the ratios of monomers taken. Quantitative treatment of the results indicates that the amide has a greater tendency to react with itself than with the nitrile (ratio of velocity constants $r = 1{\cdot}3$), the reverse being true for the nitrile ($r = 0{\cdot}88$). The results are in accord with calculations based on the polarisation (*e*) and mesomerism (*Q*) functions of Price (*J. Polymer Sci.*, **2**, 101 (1947); **3**, 772 (1948)) for the monomer molecules. The copolymer obtained from 9 parts of nitrile and 1 part of amide is suitable for fibre production, and a future paper will describe the properties of the fibre obtained. A. E. S.

Method of Preparing Spinning Solutions of Vinyl Chloride Copolymers. E. S. Roskin. *J. Appl. Chem. U.S.S.R.*, **27**, 560–562 (May 1954).

Copolymers of vinyl chloride (92%) with 8% of vinyl acetate, methacrylic acid, or butyl methacrylate form solutions, suitable for spinning into filaments, in an equimolecular mixture (5 : 7 by wt.) of the non-solvents acetone and benzene. The third copolymer can be prepared directly from the monomers in the solvent medium. A. E. S.

Glass Fibres— Chemical Characteristics and Coating Techniques. A. Marzocchi. *Amer. Dyestuff Rep.*, **43**, P 329–P 330 (24 May 1954).

New Industrial Applications of Fibreglass Textiles. R. C. Horton. *Amer. Dyestuff Rep.*, **43**, P 330 (24 May 1954).

PATENTS

Viscose Rayon containing Urea. American Viscose Corpn. *USP* 2,648,611

Adding urea to normal viscose and then extruding into an acid bath results in fibres of improved breaking toughness and average stiffness (cf. Smith, *Proc. Amer. Soc. Test. Mat.*, **44**, 589–590 (1944)). C. O. C.

Handling Viscose Rayon Cakes. American Viscose Corpn. *USP* 2,647,816

The cake is covered with a liquid-permeable protective paper-like wrapper made of a mixture of fibres which are not affected by aqueous saponifying media, and acetate rayon bonded together, the fibres being in a state of potential unbalance so that when the wrapped package is treated with an aqueous saponifying medium to decrease the ester content of the wrapper, the acetate rayon fibres are free to shrink, thus shrinking the wrapper as a whole and imparting a crêpe effect to it. Such a wrapper does not tend to slip and the package is readily handled without disturbing the surface layers of the cake. C. O. C.

Removing Salts from Polyacrylonitrile. Dow Chemical Co. *USP* 2,648,592–3

A rapid method of removing the last traces of salts from freshly coagulated and stretched polyacrylonitrile fibres or films. C. O. C.

Polyacrylonitrile Fibres. Industrial Rayon Corpn. *BP* 712,042

Dipropyleneglycol is a good coagulant for ethylene carbonate solutions of acrylonitrile polymers or copolymers as there is no transesterification with the ethylene carbonate and high tenacity fibres can be produced at high spinning speeds. C. O. C.

Acrylonitrile Polymers or Copolymers having Affinity for Acid Dyes. Société des Usines Chimiques Rhône-Poulenc. *BP* 712,235

Polyacrylonitrile or copolymers of acrylonitrile with compounds free from oxo groups, e.g. acrylamide, to which have been added an aliphatic mono- or diamine of > 9C, e.g. stearylamine, in presence of an inorganic acid have enhanced affinity for acid dyes. The addition may be made to a solution of the acrylonitrile polymer or copolymer.

BP 712,268

Aliphatic or alicylic, primary or secondary amines containing < 11C, are used in presence of an organic sulphonic acid. The affinity for acid dyes of the treated polymer rapidly decreases with increase in the number of C atoms above the limit stated. C. O. C.

Modern Trends in Papermakers' Felts (XI p. 475).
Alkaline Degradation of Polysaccharides. I— Degradation of Cotton Hydrocellulose (XI p. 475).
Investigation by the Ultracentrifuge Sedimentation Method of the Molecular Weight Distribution Function of Polyamides— I and II (XIII p. 477).
Static Electrification of Filaments (XIV p. 479).
Detection of Modification in Animal Fibres. II— Tensile Recovery at 65% R.H. (XIV p. 479).

VII— DESIZING; SCOURING; CARBONISING; BLEACHING

Theory and Practice of Enzyme Desizing. J. Voss. *Melliand Textilber.*, **35**, 762–764 (July 1954).

The heat stability of bacterial amylases is of interest in continuous desizing. A prepared and standardised farina was treated under different conditions of time, temperature, and pH with bacterial, pancreatic, and malt amylases, and the rate of starch conversion was found to increase in the same order. α- and β-Amylases were isolated from malt, in which they are present in the proportions 1 : 5 to 1 : 6. The conversion rate of α-amylase at 50°C. is several times the β value, whilst at low temperatures conversion depends almost exclusively on the α-form. Bacterial amylase was used on starch at different degrees of swelling. The results obtained confirm the practice of working at high temperatures or swelling with hot water before desizing. S. R. C.

The Washing Process. IX— Electron-microscopic Investigation of Soil on Cotton and Wool. W. Kling and H. Mahl. *Melliand Textilber.*, **35**, 640–645 (June 1954).

Different natural and artificial soiling materials in the mass and on cotton and wool were investigated by electron-microscopic studies (illustrated). By means of a special reprinting method submicroscopic soil particles were revealed and in certain cases could be characterised. The number of soil particles corresponded remarkably well with the effective degree of soiling, even with small fields of view. This led to the conclusion that the soiling was uniformly distributed and that only a limited number of photographs were necessary. S. R. C.

Textile Detergents and their Properties— II. M. Rösch. *Melliand Textilber.*, **35**, 791–798 (July 1954).

Improved washing techniques by the use of electrolytes, changes in the hydrophobic portion of detergent, variation in charge of fibre and soil, impregnation with concentrated detergent, and builders are considered, and acid washing

detergent concentration, liquor ratio, finish, e.g. starch, removal, and rinsing are discussed. S. R. C.

Tar Spot Removal from Cotton Fabrics during Finishing. J. Crompton and L. R. Hubbard. *Text. Research J.*, **24**, 578–583 (June 1954).

The problem of tar spots on cotton fabrics is discussed, and their removal by spotting techniques or by the use of soap emulsions in organic solvents after finishing is detailed. Removal of tar spots during finishing by either a pressure kier or on a quench-box procedure is also reported. A. B.

Theory of Soil–Fibre Complex Formation and Stability. J. Compton and W. J. Hart. *Text. Research J.*, **24**, 263–264 (March 1954).

Practical Aspects of Grease-wool Scouring. R. E. Wolfrom. *Amer. Dyestuff Rep.*, **43**, P 372–P 379 (7 June 1954).

The nature of detergent scouring processes, methods in common use, and laboratory test methods are briefly described, followed by a comprehensive survey of a large number of mill trials on both coarse and fine wools, using non-ionic detergents. Complete recipes and cost data are included. J. W. B.

PATENTS

Carbonising Loose Fibres. M. T. Hoffmann. *USP* 2,647,286

If the acidified fibres are heated as a thin layer the effectiveness and the speed of carbonisation are considerably increased and this results in wool of improved felting quality. Excellent results are obtained by carding the acidified fibres and then treating the resultant web. C. O. C.

Yarn Mercerising. Dixie Mercerising Co. *USP* 2,647,037

Continuous mercerising of a single two-ply yarn is described whereby increased lustre, strength and uniformity of treatment are obtained as compared with warp mercerising. C. O. C.

Ultrasonics and Sound Vibrations in Bleaching and Dyeing (VIII this page).
Experiments in Textile Chemistry using Redox Potential Measurements (VIII this page).

VIII— DYEING

Ultrasonics and Sound Vibrations in Bleaching and Dyeing. C. Weimann. *Teintex*, **19**, 437–447 (June 1954).

A review of work with piezoelectric and magnetostriction generators carried out in various countries on flax retting, suint washing of wool, and dyeing of various fibres. S. R. C.

Adsorption of Detergent in the Dyeing Process. L. Flett and L. F. Hoyt. *Amer. Dyestuff Rep.*, **43**, P 335–P 338 (24 May 1954).

Experiments are carried out to determine the amount of synthetic detergent (Nacconol NR) adsorbed by wool at different stages of the dyeing process, using Wool Orange A (*C.I.* 151). Tests are made in which the detergent is applied before, during, and after dyeing, the detergent being estimated by direct titration with a cation-active agent in presence of chloroform. (A slight modification of the usual partition titration is employed in which the chloroform layer, deeply coloured with dye–cation-active agent complex, is discarded near the end-point and replaced by fresh chloroform and a little bromophenol blue.) It is found that both the dye and the anion-active detergent are quickly adsorbed, an equilibrium state being reached in which additional detergent can remove dye already fixed to the fibre. J. W. B.

Exact Pattern of a Concentration-dependent Diffusion in a Semi-infinite Medium— III. H. Fujita. *Text. Research J.*, **24**, 234–240 (March 1954).

Variables in Padding Processes. R. W. Speke. J.S.D.C., **70**, 221–226 (June 1954).

An outline is given of the salient features governing the design of pad mangles for the application of dyes and finishing agents to woven textiles. The important manipulative variables governing the padding process— namely the effects of cloth preparation, running speed, temperature of the pad liquor, and padding oils— are described. The basic principles involved when wet fabrics are repadded are briefly surveyed. AUTHOR

Dyeing of Cellulosic Fibres at High Temperature. L. Drijvers. *Teintex*, **19**, 426–435 (June 1954).

A method is described for the dyeing of vat and direct dyes at high temperature, maintaining the concentration of colouring matter in the bath as low as conveniently possible throughout the progress of the operation. This is advantageous where the dye or leuco derivative possesses high substantivity together with a slow diffusion rate. The temperature necessary for the best dispersion may be reduced, an important advantage when using unstable dyes and auxiliaries. Theoretically, the colouring matter is added to the bath at a rate equal to the diffusion of the dye in the fibre in order to avoid too great a concentration of dye at the surface of the fibre, and at a temperature as high as conveniently possible. Direct dyes are best exhausted at the highest convenient temperature. Heavy dyeings of Class A direct dyes which exhaust on cooling should be matched at a temperature corresponding to maximum exhaustion. The process is recommended for viscose rayon cakes. S. R. C.

Developments in Dyeing Rayon-staple Fabrics with Direct Cotton Dyes and Vat Dyes. P. A. Holt. *Dyer*, **111**, 981–989 (25 June 1954): *Textil-Praxis*, **9**, 627–628 (July 1954).

About 50% of cotton fabrics in England are vat-dyed, but $< 10\%$ of rayon staple fabrics. For continuous vat dyeing, spun rayon must be thoroughly desized and not unduly stretched in the wet state. The pad–steam process is described using alkaline leuco- or vat-acid padding for light to medium depths or pigment for heavy depths, with additions of alginates and intermediate drying to prevent migration. 10–20 sec. steaming is given and cloth speeds of 46–110 metres/min. are attained. The Gen Ray process, employing pigment padding prior to reduction in a Williams unit, is mentioned. Further units may be used for oxidising and soaping, and redox potential measurement can assist in following the progress of reduction. Both pad–steam and Gen Ray processes are at least as cheap as jig dyeing in dye cost. The hot-oil and Standfast processes are referred to, as is the Bond machine, in which the fabric passes between several perforated plates through which the liquor is forced. The dyeing of rayon staple with direct dyes is usually carried out in winches, although the process is known to lead to irregularities. Continuous dyeing can be performed with well prepared cloth by padding direct dyes and steaming for 5–10 min. This overcomes variations of affinity, but dye selection, technical control, and capital outlay tend to increase dyeing costs. Crease-resisting increases the final fastness of direct dyes and may be combined with cationic fixatives in order to approach vat fastness, but costs are increased, as is the difficulty of matching. Variation in batches is reduced. S. R. C.

Experiments in Textile Chemistry using Redox Potential Measurements. J. Eisele and S. Hafenrichter. *Melliand Textilber.*, **35**, 756–762 (July 1954).

Kier-boiled cotton was treated with Na_2CO_3 (10 g./litre, 20 : 1 liquor ratio), and the effect on the change in redox potential of the system followed at 80, 90, and 100°c. in air and in nitrogen, with and without agitation, at 760 mm. and 150 mm. pressure, and with and without pulverisation of the cotton. The decomposition products are known to affect vat dyeings. The redox titration curves of Indanthren Brilliant Green 3B, Dark Blue BOA, Orange F3R, and Violet FFBN are given. High leuco potentials in general correspond to good resistance to soda-boiling, but a weighting factor based on the position of the central portion of the curve must be introduced. Vat dyes are grouped empirically into six classes according to leuco potential and weighting, the arrangement having implications for the resistance to reduction of vat dyeings. S. R. C.

Production and Properties of Solution-dyed Acetate Rayon. P. F. Flamm. *Text. Research J.*, **24**, 357–361 (April 1954).

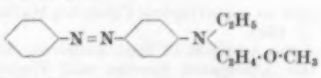
The production of solution-dyed acetate rayon is described, and the factors affecting colour uniformity are detailed. The fastness properties of this fibre are discussed. A. B.

Progress in the Dyeing of the Newer Synthetic Fibres. P. J. Choquette. *Text. Research J.*, **24**, 387–394 (April 1954).

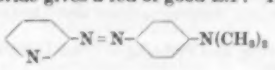
Recent developments in the dyeing of the newer synthetic fibres are discussed, including the high-temperature dyeing of Dacron polyester fibre, Orlon acrylic fibre, Acrilan acrylic fibre, dynel, wool, and nylon. The uses of carriers are detailed, together with the cuprous-ion technique, special azoic techniques, and various after-treatments. New methods of fibre-mixture dyeing are discussed. A. B.

Problems of Dyes for Synthetic Fibres. J. Wegmann. *Textil-Rund.*, **9**, 341–348 (July 1954).

On Orlon, the dye—



gives a yellow of very poor fastness to light (L.F.) whilst its hydrochloride gives a red of good L.F. The dye—



produces a brown of poor L.F., but its violet salts yield very fast dyeings. The latter are fast to NaOH, but not to ammonia. Orlon itself can act as the acid, as the base of Diorlin Brilliant Blue RL gives a dyeing corresponding to about half the strength obtained normally with the salt. Diorlin (Ciba) dyes form a range of six basic dyes for application to Orlon. They reserve wool and silk well, and have good to very good L.F. Patterns illustrate the dyeing and printing of these dyes on to Orlon, and dyeing on to Crylor–wool mixture. Similar ranges are Du Pont Basic (DuP), Acrylosol (G), and Astrazone (IG) dyes. The dyeing of polyvinyl chloride and polyester fibres is also discussed briefly. H. E. N.

Problems in Dyeing the Newer Synthetic Fibres. I. M. S. Walls. *J. Textile Inst.*, **45**, P 258–P 271 (June 1954).

The chemical structure of the newer synthetic fibres is outlined, and classes of dyes which can be used to dye them are described, together with dyeing methods, including the use of carriers. J. W. B.

Investigations on the Dyeing of Hydrophobic Fibres. T. Vickerstaff. *Melliand Textilber.*, **35**, 765–772 (July 1954).

Certain fibres, e.g. polyvinyl chloride and polyethylene, are deficient in dyeing sites and call for the presence of a copolymer or new dyes of specific affinity. Fibres specially made for high tenacity, e.g. Terylene and Orlon, are compact. Increases in dyeing rate could be effected by reduction in molecular size of the diffusing bodies, increase in bath temperature, or fibre-swelling and -loosening auxiliaries. Disperse dyes show diffusion rates in Terylene and cellulose acetate of 1 : 500, and give only light to medium depths on the former. Dye components of low molecular volume can be used to form colouring matters *in situ*. Neutral dispersions of amine bases, which show affinity for Terylene by possible hydrogen bonding with ester groups, may be dyed together with 3:2-hydroxynaphthoic acid by one- or two-bath techniques to give colouring matter in the fibre after diazotization and coupling at 85°c. Vinyon, Orlon, Terylene, cellulose acetate, and polyvinyl chloride exhibit relatively high negative potentials, which hinder the access of anions. Dyeing in concentrated electrolytes, e.g. indigoid vat dyes in K_2CO_3 or the Cu-ion technique, overcomes the barrier with Orlon.

In all known dyeing processes, temperature elevation increases diffusion, activation energy of dye, dyeing, and levelling. Thermal agitation of chains may also give transient gaps in the Terylene structure, through which the dye diffuses. Pressure vessels at 130°c. are used for yarn; enclosed jigs and the Barotor for cloth. An extreme example of high-temp. dyeing is the Thermosol process— several seconds at 200–220°c. Excellent laboratory results have been obtained in saturated steam for 3 min. at 120°c.

The action of "carriers", a deprecated term since it suggests a complex of high molecular volume, is still unexplained, particularly because of lack of constitutional similarity (phenols, amines, acids, aromatic and chlorinated aromatic hydrocarbons, esters and ethers). The theoretical possibilities of operation are increasing the dye solubility in the aqueous phase, aqueous swelling of the fibre, plasticisation of the fibre, and creation of new dyeing sites. Experimental work suggests, however, that soluble auxiliaries, e.g. phenol, must have low molecular volume and affinity for the fibre, and though they compete with the dye for dyeing sites, the dyeing process is accelerated possibly by swelling or molecular softening of the fibre. Unless pressure vessels are used, however, the high volatility of such compounds leads to irregular results in practice. Soluble auxiliaries, e.g. diphenyl, rapidly saturate and swell the fibre, and subsequently concentrate at the surface; since the dye is more soluble in the auxiliary than in water, the fibre is bathed in a concentrated dye solution and dyeing is accelerated. S. R. C.

Relationship between Structure of Dyes and their Dyeing Characteristics on Hydrophobic Fibres AATCC Northern New England Section. *Amer. Dyestuff Rep.*, **43**, P 426–P 437 (5 July 1954).

A study is made of the dyeing behaviour of disperse (acetate-rayon), basic, special basic, milling acid, and premetallised dyes on dynel, Dacron, Acrilan, and Orlon, and the results are compared with similar dyeings on acetate-rayon and nylon fibres. From a consideration of chemical constitutions it is concluded that disperse dyes have affinity for all the fibres; many basics, a good affinity for only some of the fibres; and acid dyes for still fewer. Hydroxyl groups (and perhaps ketonic groups because of tautomerism to hydroxyl) appear to impart affinity, which is lowered by sulpho and carboxyl residues. J. W. B.

Significance of the Diffusion Coefficient in the Dyeing of Polyamides. B. Kramer. *Melliand Textilber.*, **35**, 518–523 (May), 651–656 (June 1954).

Elementary principles are first explained and then the method employed for determining the diffusion coefficients (D) of dyes is described. Small blocks of polymer (Ultramid 6A, formerly Igamid 6A, a mixed polymer of hexamethylenediamine diadipate and ε-caprolactam) are dyed, and then cut by means of a microtome into sections ca. 50 μ. thick. The penetration of dye is determined using a microscope (magnification $\times$ 34), and from the average of 10 measurements D is calculated. A table lists D of 10 disperse dyes (Perliton, Basf) at 60, 80, and 100°c. D of the Yellow 3G and Brilliant Blue B are less than half those of the other dyes. D are useful in selecting dyes for compound shades. From the temp. dependence of D the apparent activation energies of diffusion are calculated. In general, the greater the number of atoms per molecule the greater is D; but for molecules containing the same number of atoms, anthraquinone dyes diffuse more rapidly than diphenylamine or azo dyes. D, together with the ionic charge and the mol. wt. of 12 acid dyes (Telon, FBy) are tabulated. In general, sulpho groups reduce D, but sufficiently basic amino groups counter their effect. D of these acid dyes are mostly smaller than those of disperse dyes. For both classes of dye, penetration and equalisation are shown to be directly, fastness to washing inversely, related to D. H. E. N.

Dyeing of Orlon, Dacron, and their Mixtures with other Fibres. J. F. Laucius and P. L. Meunier. *Textil-Praxis*, **9**, 623–624 (July 1954).

A short review of the available techniques. S. R. C.

Potential Dyeing Methods for Polyacrylonitrile Fibres. W. Kunze. *Textil-Praxis*, **9**, 660–662 (July 1954).

A number of commercial fibres are tabulated. These may be differentiated by cutting cross-sections, of which illustrations are given. As a class, the fibres may be identified by the presence of a CN group, e.g. by heating

and allowing the vapour to meet one drop of cold, saturated benzidine acetate–copper lactate solution on filter paper. HCN gives a strong blue colour. The dyeing of polyacrylonitrile fibres with acid, basic, indigoid vat, disperse, and Anthrasol dyes is discussed. S. R. C.

Dyeing and Finishing Orlon Acrylic Fibre. R. F. Stevens. *Amer. Dyestuff Rep.*, **43**, P 409–P411 (21 June 1954).

Procedures are given for dyeing Type 42 Orlon, with reference to stock, top, yarn, sweater and half-hose, five-gauge jersey, woollen and worsted blends, and rayon blends. A bleaching treatment entails the use of 1·5 g. Textone and 1·0 g. nitric acid per litre at 180°C. for 1 hr., a less brilliant but more durable white being obtained by 30 min. boiling in 0·1% oxalic or 0·1% of 70% hydroxyacetic acid. J. W. B.

Theory of Dyeing of Paper. C. Faure and F. Giot. *Assoc. tech. ind. papetière, Bull.*, 31–7 (1954): *Chem. Abs.*, **48**, 7299 (25 June 1954).

An outline of the conditions required to fix acid, basic and direct dyes on paper and of pigment retention. The influences of the chemical components and the fine structure of the pulp and of the structure of the dyes in their retention by pulp are described. C. O. C.

Mechanism of Leather Dyeing. W. K. Schweitzer and R. M. Lollar. *J. Amer. Leather Chem. Assocn.*, **49**, 390–404 (May 1954).

Calfskin is chrome-tanned in four ways, and dyeing studies are carried out using Orange II (*C.I.* 151), Orange I (*C.I.* 150), Fast Red A (*C.I.* 176), and a dye synthesised in the laboratory, with a high sulphonic acid content (sulphanilic acid → β-naphthol-4:6:8-trisulphonic acid). Results indicate that dyeing with simple monoazo anionic dyes proceeds in two stages, firstly take-up of dye and secondly fixation of dye on leather. In the competition for the dye between solvent and leather, increasing the number of solubilising groups favours the solvent, as does reducing the number of sites in the leather, either by decreasing the negative charge or by increasing the difficulty of complex penetration. Penetration of dye into the chrome complex and leather–dye hydrogen bonding are very important. Electrostatic bonding plays a part, but does not appear necessary in all cases. J. W. B.

Colour Fastness and Textile Finishing Requirements of the Ultimate Consumer. J. S. Ingham. J.S.D.C., **70**, 227–229 (June 1954).

A large retail organisation quickly obtains the public's reaction towards visible factors of style and colour. An attempt has been made in the laboratory to obtain some information on the invisible factors of durability and wearability. From a survey and laboratory findings, it is clear that certain standards must be achieved to meet the demands of the public. This paper deals with some of these findings and observations in the field of dyeing, printing, and finishing. Further, the information has been passed on to dyers, finishers, and dyemakers, and the gaps in production have been pointed out which it would be very desirable to fill to meet the public's demand. AUTHOR

Fastness to Organic Solvents. C. H. Fischer-Bobsien. *Z. ges. Text. Ind.*, **55**, 127 (1953): *Textil-Rund.*, **9**, 337 (June 1954).

In dry-cleaning, the solubility of red and bordeaux dyes (particularly azoic combinations) applied to raincoats proved very objectionable. Amongst other data, 15 advantageous azoic combinations are listed. Lack of fastness to organic solvents can lower the serviceability of textiles, and further consideration of this point, particularly in dyemakers' literature, is advocated. H. E. N.

PATENTS

Dyeing Cellulose Ester or Ether Fibres with Haematein. Societe Rhodiaceta. *BP* 712,460

Deep blacks of excellent fastness, particularly to rubbing, are obtained by chroming at 75–80°C. in a liquor kept at pH 4·0–5·5 and containing ≮ 10 g./litre of NaCl, Na_2SO_4, Na acetate or monosodium orthophosphate. C. O. C.

Hair Dyeing. Lever Brothers & Unilever. *BP* 712,451

Alkaline pre-treatment can be omitted, even in the case of coarse hair, when using oxidation dyes if there is incorporated in the composition a water-soluble aliphatic polyhydroxy compound, e.g. sorbitol, and an alkanolamine (alkanol of < 7C), e.g. triethanolamine. The pH of such composition can be considerably reduced, e.g. with NH_4 ions, and this enhances even dyeing. C. O. C.

Dyeing Polyamides and Polyurethans with Nitroso Dyes. Basf. *BP* 711,766

The complex metal derivatives of hydroxynitroso compounds free from SO_3H groups, e.g. the iron complex of 1-nitroro-2-hydroxynaphthalene, dispersed in an aqueous solution of an alkyl-naphthalene sulphonic acid or an ethylene oxide condensate are used to dye nylon or polyurethans. Dyeing is conducted at the boil, and the bath exhausted by adding $(NH_4)_2SO_4$, to produce greens. R. K. F.

Alkylamine Alginate Thickeners for Aqueous Alcoholic Dyebaths or Printing Pastes. Celanese Corpn. of America. *USP* 2,647,035

Aqueous alcoholic dyebaths or printing pastes thickened with 0·1–10·0% of an alkylamine alginate, e.g. dibutylamine alginate, are stable and do not tend to foam. The alginate is readily removed from the dyed material by washing with hot water. C. O. C.

Action of Light on some Organic Colouring Matters— I and II (IV p. 459).
Influence of the Addition of High-molecular Electrolytes upon the Absorption Spectra and Fluorescence of Organic Dyes— II and III (IV p. 459).
Handling Viscose Rayon Cakes (VI p. 469).
Pigmented Prints, Impregnations and Coatings (IX this page).
Finishing, Dyeing, and Printing of Glass Decorative Fabrics (X p. 474).

IX— PRINTING

Fundamentals of Colour Reproduction. R. W. G. Hunt. *Nature*, **174**, 12–16 (3 July 1954).

An outline of the development of the principles of colour photography is given. This includes an account of the Lipmann interference method of reproducing colour by physical means. A comparison is made between the early development of colour photography and the present development of colour television by additive methods, while present-day colour photography is almost exclusively by the subtractive system. The accuracy of colour reproduction is discussed in an elementary manner and the reasons for the deficiencies are described. It is concluded that the present-day technically very poor reproduction of colour is commercially tolerated only because the average viewer very rarely makes a direct comparison between the original and the reproduction. W. J. M.

Studies in Blue Print. I— Mechanism of Photochemical Reaction of Complex Iron Salts. S. Suyuki. *J. Chem. Soc. Japan*, Ind. Chem. Sect., **55**, 755–7 (1952): *Chem. Abs.*, **48**, 7463 (10 July 1954).

$Na_3[Fe(C_2O_4)_3]$ and the corresponding ammonium compound when illuminated by mercury tungsten light showed photoconductivity whereas the corresponding K salt did not. This conductivity is ascribed to electron transfer in $[Fe^{3+}(C_2O_4)^{2-})_3]^{3-}$ which suggests that in the primary process of blue-print formation, Fe^{3+} is reduced to Fe^{2+} to produce Turnbull's Blue. Qualitative explanation is attempted on similar lines of the reversal phenomenon which occurs when the blue print is exposed to excessive light energy. C. O. C.

PATENTS

Printing with Mordant Dyes. ICI. *BP* 712,428

Precipitation is avoided in mordant dye printing pastes by using as thickener a water soluble salt of a carbohydrate carboxylic acid and incorporating in the paste a sequestering agent. C. O. C.

Pigmented Prints, Impregnations and Coatings. Basf. *BP* 712,128

When using the process of *BP* 709,954 (J.S.D.C., **70**, 425 (Sept. 1954)) prints and dyeings of improved fastness to washing are obtained by using instead of water-insoluble polymers which are inert to cross-linking agent, emulsions which contain in the outer aqueous phase a dispersion or a solution of a film-forming linear macromolecular substance having reactive groups able to react with the cross-linking agents. This enables water-soluble or strongly-swelling polymers to be used, e.g. polyvinyl alcohol, polyacrylates or poly-*N*-vinyl-2-pyrrolidine. C. O. C.

Metallised Patterns on Fabrics. P. Lebuy. *BP* 712,437

One side of the fabric is printed with a driable composition. Then, before the composition has dried, the printed side is treated with a jet of air containing metal particles in suspension while simultaneously air is passed through the fabric from the non-printed side. This prevents the metal penetrating into the interstices of the fabric and of the yarns of which it is made. C. O. C.

Printing of Aromatic Polyesters. ICI. *BP* 712,418

Terylene and similar polyesters are printed with a vat dye, steamed in acid or neutral medium in presence of a reducing agent, and then oxidised. Prints of greater depth and a wider range of colours than has hitherto been possible on these materials are obtained. C. O. C.

Alkyldiformylphenylenediamines— Solubilising Sulphuric Esters of Vat Dyes in Printing Pastes. General Aniline. *USP* 2,647,815

Compounds of formula—

(R^1 = Alk or hydroxyalkyl; R^2 = Alk, hydroxyalkyl or H) are useful in solubilising sulphuric esters of vat dyes in aqueous printing pastes etc. A mixture of *NN'*-dimethyl, *NN'*-diformyl-*p*-phenylenediamine; *NN'*-diethyl, *NN'*-diformyl-*p*-phenylenediamine and *N*-methyl, *N'*-ethyl, *NN'*-diformyl-*p*-phenylene diamine, in which the groups CH_3:C_6H_3::1:3, is especially useful. C. O. C.

Daylight Fluorescent Prints. J. L. Switzer and R. C. Switzer. *BP* 713,073

The pattern is printed on the material with an adhesive, the depth of the coating being 0·001–0·003 in. A dry pigment, flock, dust or the like containing a fluoragent having daylight fluorescence is then applied, the optimum effect being obtained when 0·00006–0·00003 g. fluoragent is applied per sq. cm. of surface at a concentration of 0·01 g. per c.c. of coating. C. O. C.

Printing on Polyethylene or like Plastic Substance to which Printing Inks adhere poorly. B. Winstone & Sons. *BP* 712,838

After the material has been printed, preferably screen printed as this leaves a thicker film of ink than other methods, it is coated with a transparent substance to which both pressure sensitive adhesive and water-moistened types of adhesives, tapes and papers do not cohere, e.g. a silicone wax or oil such as DC7 or DC200. C. O. C.

Printing on Polyethylene. Traver Corpn. *USP* 2,648,097

Polyethylene is rendered highly receptive to common ink and coating compositions by directing a gas flame onto it for a brief period without raising the mass to a temperature enabling distortion. If the flame is at 1300–1600°F. the ink-receptive surface is formed instantaneously. C. O. C.

Prewetting in Imbibition Printing. Technicolor Motion Picture Corpn. *USP* 2,648,280

Apparatus for prewetting a film blank before it is brought into contact with the coloured matrices and which eliminates streaking and blurring of previously imbibed dye. C. O. C.

Photographic Colour Correction Process. DuP. *BP* 714,012

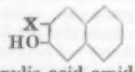
A colour correction mask is formed in a colour photographic element in which at least one water-permeable layer contains a colour subtractive image in quinoneimine or azomethin dye, residual colourless colour former and a colourless primary aromatic amine incapable of reacting with the oxidation products of an aromatic primary amino developing agent to form a dye, is treated simultaneously or successively with aqueous acid and a nitrite so as to diazotise the amino group and cause it to couple with the colour former. C. O. C.

Multicolour Photographs. I. O. Ball. *BP* 714,243

A five-component substractive colour reproduction process comprises the exposing of five light-sensitive photographic layers to produce five colour separation negatives through light filters which produce predominant exposure in the ranges 425–445, 610–650, 472–492, 525–545 and 564–584 mμ. respectively and which have transmission band widths $\geq$ 60 mμ. at one half the transmission. C. O. C.

Diazotypes. Chemische Fabriek L. van der Grinten. *BP* 713,917

Diazotype copies are produced by selectively exposing, e.g. through a continuous tone diapositive, a one-component diazo film layer material containing a *p*-tertiary-aminobenzene diazo compound whose amino group is substituted by radicals together containing $>$ 6C and which yields an active photochemical decomposition product. It is then treated with a developer containing an azo coupling component of formula—



(X = OH or a carboxylic acid amide group in which the amide radical contain substituents other than aromatic radicals). This results in images in which the medium tones, particularly those in the dense areas, have richer graduation than is usually obtained with other azo coupling components. C. O. C.

Photolithographic Diazotype Printing Materials and Processes. Kalle & Co. *BP* 712,606

Colour Fastness and Textile Finishing Requirements of the Ultimate Consumer (VIII p. 472).
Alkylamine Alginate Thickeners for Aqueous Alcoholic Dyebaths or Printing Pastes (VIII p. 472).
Finishing, Dyeing, and Printing of Glass Decorative Fabrics (X p. 474).
Transfer Sheets for Use with a Receiving Sheet Sensitised by a Colour-reactant Substance (XI p. 476).
Thermoelectric Potentials of Dye–Gelatin Phosphors (XII p. 476).

X— SIZING AND FINISHING

Economies in Cylinder Drying. P. W. Troschin. *Tekstil. prom.*, **14**, 42 (March 1954): *Textil-Praxis*, **9**, 559–561 (June 1954).

The steam consumption of a cylinder-drying set can be reduced and the production increased by the use of hot (50–60°C.) rinsing waters, which may be heated by exhaust steam. After hot rinsing, the material should be mangled before presentation to the cylinders, with the nip as close as possible, for maximum steam economy, to the first unit. Using rinsing water at 60°C. with a pad or mangle situated 5–15 m. from, and in tandem with, the drying range, the production of the latter can be increased by 15–25%. The principles involved are treated mathematically, allowing the potential saving under a given set of conditions to be estimated. S. R. C.

Consumption of Steam and Electric Current by Driers. H. Vits. *Melliand Textilber.*, **35**, 556–558 (May), 659–662 (June 1954).

A discussion of driers using tables previously published (*J.S.D.C.*, **69**, 516 (1953)). In an air-drier of older design, per kg. of water evaporated, 3 kg. saturated steam at 6 atm. (1500 kg.cal.) and 0·1 kWh. electricity (86 kg.cal.) are required. The cost of the latter is about 17% of the former. The total heat is used as follows— 650 kg.cal. for evaporating, including 20 kg.cal. for the heating of the fabric; 420 kg.cal. lost in heated air in the exhaust; 300 kg. cal. lost through the walls of the drier; 100 kg.cal. lost through parts not insulated; and 85 kg.cal. carried away, e.g. by stenter-clips. A hot-steam-drier of new design requires, per kg. of water evaporated, 1·45 kg. saturated steam at 6 atm. (725 kg.cal.) and 0·06 kWh. electricity (52 kg.cal.). The figures for the uses of this heat corresponding to those above are— 650, 30, 50, 30, and 30 kg.cal. (N.B. sum = 790 kg.cal.). The same dryness of fabric is achieved at higher temp. at a higher R.H. When dried in a hot-steam-drier, using temp. of 130–150°C. for the steam–air mixture, as long as the fibres are saturated, their temp.

will not exceed the condensation temp. (wet-bulb temp.). When the fibres begin to dry, their temp. will increase, but since the degree of dryness required is not that which would be in equilibrium with the steam–air mixture, their temp. lies between the condensation and the actual temp., in practice hardly exceeding 100°C. H. E. N.

Finishing of Fabrics. H. C. Borghetty. *Text. Research J.*, **24**, 383–386 (April 1954).

Various types of finish are discussed, in particular reactant resins such as urea–formaldehyde or melamine–formaldehyde. A. B.

Dissolution of Cellulose in Cupriethylenediamine Solution—Effect of Mercerisation. R. H. Andersson and O. Samuelson. *Svensk Papperstidning*, **57**, 459–464 (15 July 1954).

The dissolution of cellulose in cupriethylenediamine solution of various concentrations was studied, sulphite and cotton linters pulp, rayon and hydrocellulose treated with warm alkali, as well as mercerised samples of the pulps, being used. For all the samples, mercerisation resulted in a lower solubility in cupriethylenediamine, although an enhanced reactivity (degree of substitution) was observed. This indicated that mercerisation and the accompanying increase in the reactivity of the cellulose correspond to a macro-heterogeneous course of reaction. S. V. S.

Antistatic Textile Finishes. M. Hayek. *Amer. Dyestuff Rep.*, **43**, P 368–P 371 (7 June 1954).

A review is given of the nature of static on textiles, the mode of action of antistatic agents, the relation between antistatic action and chemical structure, and the requirements and properties of antistatic agents. J. W. B.

Stabilising Viscose Rayon Fabrics. L. L. Walmsley. *Amer. Dyestuff Rep.*, **43**, P412–P415 (21 June 1954).

The shrinkage of viscose rayon fabrics, six stabilising processes, and the stabilising of knit goods, are discussed. J. W. B.

Fundamental Considerations of the Crease-resisting of Cellulosic Fabrics. C. van Bochove and G. J. Schuringa. *Teintex*, **19**, 505–518 (July 1954).

A distinction is drawn between resistance to creasing, which depends on rigidity, and crease recovery, depending on elasticity. Percentage recoveries after 4% extension are quoted—viscose rayon 30–74, cotton 50, wool 80–90, nylon 100, and Orlon 84. The resin treatments with urea–formaldehyde, etc. and cross-linking with formaldehyde and with glyoxal are considered. Adipamide–formaldehyde is claimed to have a fastness to washing superior to urea–formaldehyde. There are 34 references. S. R. C.

Present State of Water-repellent Finishing—I and II. R. Keppler. *Textil-Praxis*, **9**, 577–580 (June); 646–649 (July 1954).

Tests of water-repellency are briefly described, and the methods of proofing classified as—(i) esterification, (ii) etherification, (iii) one-bath, (iv) two-bath, (v) resin, and (vi) silicone processes. The use of stearyl chloride, organic peroxides, *N*-*n*-octadecyl-*NN'*-ethyleneurea, *N*-hydroxymethylstearamide, and distearamide are discussed under (i). Under (ii) are described octadecyl and dodecyl chloromethyl ether and compounds of general formula—

$$(X{\cdot}A{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}O)_m R(O{\cdot}CO{\cdot}NH{\cdot}CH_2OH)_p$$

(R = organic grouping, e.g. substituted aliphatic; A = aliphatic or heterocyclic tertiary amine; and X = an acid anion). S. R. C.

Washing Fastness of One-bath Waterproofs. G. Wittmann. *Textil-Praxis*, **9**, 545–546 (June 1954).

The effects of waterproofing agents on air-porosity, handle, and colour are discussed. A good fastness to soap washing can be obtained with heat-labile products which deposit hydrophobic residues, or with silicones; but, owing to the number and the variety of detergents used in laundering, and to their partial substantivity, absolute fastness to washing cannot be claimed. S. R. C.

Resistance to Microbiological Deterioration of Resin-treated Cellulosic Fabrics. T. F. Cooke. *Text. Research J.*, **24**, 197–209 (March 1954).

It is shown that the thermosetting, aminoplast textile resins provide excellent resistance to the cellulolytic micro-organisms. These resin treatments have the advantages over the normally used toxic inhibitors of being completely resistant to leaching, and non-dermatitic. Durable water-repellent and fire-resistant treatments can be incorporated with these resins to provide these properties in addition. A. B.

Ultraviolet-screening Properties of Certain Pigment–Vehicle Combinations. L. L. Heffner. *Text. Research J.*, **24**, 272–278 (March 1954).

It is shown that untreated cotton duck is quickly damaged by outdoor weathering, and that effective additive finishing can greatly reduce this degradation. A. B.

Stability to Water Leaching of some Textile Fungicides applied to Unlined Flax Forestry Fire Hose. G. R. F. Rose and C. H. Bayley. *Text. Research J.*, **24**, 229–234 (March 1954).

Of various fungicides tested for stability to leaching, those containing copper were the most satisfactory, in particular copper 8-hydroxyquinolinolate, which has surprisingly high efficiency in very small amounts. A. B.

Flameproofing with Tetrakishydroxymethylphosphonium Chloride (THPC). W. A. Reeves and J. D. Guthrie. *Dyer*, **111**, 567–570 (16 April 1954): *Ind. Eng. Chem.*, **46**, 17A–18A (June 1954): O.T.S. (Washington) IR 11318 (1954): D.S.I.R. TIDU 0792/38.

A finish which is flameproof, free from afterglow, and resistant to repeated laundering, may be applied to cotton goods by means of a soln. containing ca. 16% THPC, 9·5% trimethylolmelamine, 10% urea, and 3% triethanolamine. In a typical laboratory-scale application to an 8-oz. cotton twill, the goods were padded using 2 dips and 2 nips with tight setting (giving a wet pick-up of 71·5%), dried for 4·5 min. by passing through a forced-draught oven at 185°F., cured for 4·5 min. in the same way at 285°F., washed in cold water and then in a hot detergent soln., and finally oven-dried. The THPC copolymerises with the trimethylolmelamine to give an insol. resin inside the fibres. Free HCl liberated during the reaction is taken up by the urea, and the actual amount required must be determined experimentally, since some is decomposed during the cure and some combines with the THPC to become part of the polymer. Triethanolamine stabilises the resin soln., which tends otherwise to polymerise and to gel within a few hr. even at room temp. The amount of resin required to give effective flameproofing varies from ca. 10% for a 32-oz. duck to ca. 32% for a 2-oz. marquisette, and may best be varied by varying the concn. of the padding soln. It is best to treat the finished, dried fabric with a softener in order to restore the slight loss in tear strength brought about by the proofing treatment; waterproofing treatments (with which the THPC finish is fully compatible) may serve in this capacity. There is evidence that the THPC treatment also enhances the crease- and shrinkage-resistance of fabrics, and protects them against attack by micro-organisms. THPC is synthesised from phosphine, formaldehyde, and HCl. J. W. D.

Finishing, Dyeing, and Printing of Glass Decorative Fabrics. R. F. Caroselli. *Amer. Dyestuff Rep.*, **43**, P327–P328 (24 May 1954).

A process, termed *Coronising*, is described in which woven Fiberglas fabric is passed for 5–15 sec. through an oven at 1200°F., where fibres and weave are set and sizes or other organic materials are burned off the glass. Wrinkle resistance is also imparted. A resin finish, which can include pigments, is then applied on a padder and set in an oven at 320°F. The material is finally padded with stearatochromic chloride, which, when dried at 340°F., bonds the finish to the glass and ensures the best possible abrasion resistance. J. W. B.

PATENTS

Reducing the Felting Power of Wool. Ciba. *BP* 711,861

The wool is treated with aqueous chlorine, hypochlorous acid or a hypochlorite, in presence of a water-soluble methylol compound of a diamino-1:3:5-triazine containing no reactive substituents except amino groups. This improves the evenness of chlorination. C. O. C.

Resin Finish for Regenerated Cellulose Fabrics. Tootal Broadhurst Lee Co. *BP* 713,001–2

When baking cellulose and regenerated cellulose fibres which have been impregnated with urea or melamine–formaldehyde precondensates the molecular proportion of formaldehyde to urea can be raised above 1·6:1 if the

atmosphere in the baking stove contains < 10% of superheated steam. The finished material has greater resistance to abrasion than that baked in absence of superheated steam. C. O. C.

Crease-resisting Finish. Tootal Broadhurst Lee Co. *BP* 712,098

The materials are impregnated with both crystalloidal and colloidal amino-aldehyde condensates followed by curing to form a resin. The treated materials have better tensile strength, abrasion resistance and wet crease resistance than if crystalloidal condensates alone had been used. C. O. C.

Pile Fabric. Dunlop Rubber Co. *BP* 712,251

A backing fabric is coated with a vinyl polymer, a plasticiser which gels the polymer when heated, and a dehydrating agent which absorbs water at the temperature of gelation of the polymer. Fibres are then applied to the coating and the whole heated to gel the polymer and anchor the fibres in it. C. O. C.

Films having a Matt, Porous and Non-adherent Surface—Coating Agents for Fabrics. Basf. *BP* 712,129

Matt, porous films having a non-adherent surface are produced by applying a polyvinyl chloride paste which does not gel until heated to which has been added fillers containing in a physically combined form a liquid which is a non-solvent for the plasticiser and which is volatile at ordinary gelling temperature, e.g. water, and then heating to gelling temperature. They are particularly suitable for coating fabrics. C. O. C.

Glass Heat Exchanger (I p. 455).
Pile Fabric (I p. 455).
Occurrence, Behaviour, and Elimination of Static on Textiles (VI p. 466).
Factors affecting the Tear- and Water-resistance of Lightweight Clothing and Tentage Fabrics (VI p. 466).
Morphological and Chemical Examination of Wool— I and II (VI p. 467).
Dyeing and Finishing Orlon Acrylic Fibre (VIII p. 472).
Colour Fastness and Textile Finishing Requirements of the Ultimate Consumer (VIII p. 472).

XI— PAPER AND OTHER CELLULOSIC PRODUCTS

Modern Trends in Papermakers' Felts. E. Race. *Svensk Papperstidning*, **57**, 353–362 (31 May 1954).

Synthetic wet felts, wool–synthetic fibre mixtures, the chemical modification of the wool molecule, and advances in dry felt manufacture are discussed. S. V. S.

Preformed Cleavage-plane Systems in Native Cellulose Fibres. H. Dolmetsch. *Melliand Textilber.*, **35**, 721–725 (July 1954).

Two cleavage-plane systems approximately perpendicular to each other and arranged in periodic planes at right angles to the fibre are known to exist. These are illustrated with spruce sulphite cellulose, treated with various reagents. S. R. C.

Electron Diffraction Diagrams of Cellulose Microfibrils in *Valonia*. R. D. Preston and G. W. Ripley. *Nature*, **174**, 76–77 (10 July 1954).

Electron diffraction diagrams indicate that the molecular chains of cellulose lie along the length of microfibrils in *Valonia*. Orientation of microfibrils appears to be maintained over the whole range of water content. Results agree with the view that the wall of *Valonia* consists of two sets of lamellae crossing at an angle of 60–90°. W. R. M.

Adsorption Reactions in the Steeping of Cellulose. J. Schurz. *Svensk Papperstidning*, **57**, 399–404 (15 June 1954).

The adsorption of glucose and hemicellulose in NaOH soln. on charcoal obeys Freundlich's rule. If linters cellulose is steeped in lye containing hemicellulose, negative adsorption takes place. It is considered that NaOH and H_2O from the lye penetrate the cellulose fibres by dialysis, causing them to swell, and this removal of solvent from the steeping lye raises its hemicellulose concentration. It is concluded, therefore, that the hemicellulose in the lye is not adsorbed on the cellulose. S. V. S.

Alkaline Degradation of Polysaccharides. I— Degradation of Cotton Hydrocellulose. H. Richtzenhain, B. O. Lindgren, B. Abrahamsson, and K. Holmberg. *Svensk Papperstidning*, **57**, 363–366 (31 May 1954).

The alkaline degradation of cotton hydrocellulose of varying degrees of polymerisation by 0·5 N-NaOH at 100°C. has been studied. The importance of the aldehydic end-groups for the degradation was shown by the reduction of them with Na borohydride, whereby the material was stabilised against alkali. It can be assumed that the fraction of the material which is in less ordered ranges can be degraded by alkali. The alkali-stable fraction of the limit hydrocellulose (ca. 45%) has about the same X-ray diagram and partition curve as the hydrocellulose. After precipitation of the fraction from a "cuproxam" solution or an alkaline solution, the greater part of it is still stable to alkali. On the other hand, it is degraded by alkali after a fresh hydrolysis. S. V. S.

Alkaline Degradation of Polysaccharides. II— Degradation of Hemicellulose. H. Richtzenhain and B. Abrahamsson. *Svensk Papperstidning*, **57**, 538–541 (15 Aug. 1954).

The alkaline degradation (0·5 and 1·0 N-NaOH at 100°C.) of the following carbohydrates was investigated—β-cellulose from strong spruce sulphite pulp, hemicellulose preparations from spruce holocellulose and beech xylan—the alkali consumption, the amount of undegraded polysaccharides, and the variation in the composition of the samples during degradation being determined. Mannan is degraded more readily than glucosan, which is easier to degrade than pentosan. To account for the degradation stopping before all the polysaccharides are degraded, it is assumed that the reducing sugar unit at the end of a polysaccharide chain can be stabilised by some rearrangement which obstructs the degradation of the chain. S. V. S.

Sulphate Ester of Unstabilised Cellulose Acetate. K. Keirstead and J. Myers. *Canadian J. Chem.*, **32**, 566–580 (June 1954).

Evidence for the existence of the ester form of the sulphate in unstabilised cellulose acetate has been examined by ion-exchange studies on fibrous cellulose acetate. The equilibrium reached during ion exchange is affected by the pH and by the concn. of the salt soln. used. The thermal stability of the ester varies inversely with the sulphate content. The accuracy of the various analytical methods used has been studied. J. W. D.

PATENTS

Coating Paper. A. R. Trist. *BP* 713,765

Paper to be coated is smoothed by temporarily depressing the surface fibres, a controlled quantity of coating material is applied, and the exposed surface of the layer of coating is finally polished by treating with flexible trailing blades operating in conjunction with a resilient bed after the coating material has been matured by jets of air or by radiant heat. Both sides of the web may be coated in turn and the operations are carried out in a timed sequence. S. V. S.

Safety Paper. C. Burgo. *BP* 713,351

Safety paper sensitive to all chemical reagents, particularly suitable for cheques, paper currency and the like, contains a special type of mottling obtained by adding only a very small amount of cellulose, natural, artificial or animal fibres of the same colour as the base of the paper, but previously treated with fluorescent substances specially sensitive to the chemical reagents which either cause disappearance of the mottling or produce colourings or spots easily visible under ultraviolet radiation. S. V. S.

Coating Paper. Mead Corpn. *USP* 2,647,842

Apparatus for applying a coating which is suitable for machine printing without being supercalendered. C. O. C.

Coating Paper. Combined Locks Paper Co. *BP* 712,564

Paper has a measured uniform heavy film of liquid coating material applied to one side of it at a nip between a hard-surfaced roll and a soft-surfaced backing-up

roll. The paper is moved with the roll while being held to it by the tension in the web and the action of the coating material. The paper is then passed through a second nip between the hard-surfaced roll and a soft-surfaced second coating roll, the first roll acting as a backing-up roll to apply a second film of the coating material to the other side of the web, the film being pressed against the paper before it leaves the second nip. An angular spacing of less than 180° between first and second nips prevents hydro-expansivity wrinkles from forming. The rolls are under separate speed control. S. V. S.

Coated Paper. Champion Paper & Fibre Co. *BP* 712,717

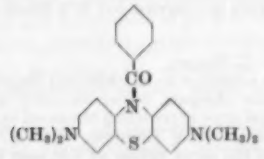
In manufacturing cast surfaced coated paper by pressing coating, e.g. mineral pigment and aqueous adhesive, carried on one side of a web of paper whose surface is in a plastic condition, on to a finished casting surface, rendering the coating non-plastic, and thereafter removing the coated paper from the casting surface, improvement is brought about by plasticising the surface portion of the dried coating by applying rewetting liquid to it, confining the rewetting and plasticising action to the surface portion of the coating, and keeping the body of the coating non-plastic at the time the coating is pressed against the casting surface. The rewetting liquid is applied from a pool in a press roll nip immediately before the coated paper is pressed on to the casting surface. This prevents penetration and appreciable moistening of the paper. S. V. S.

Silicate-coated Papers. Philadelphia Quartz Co. *USP* 2,647,069

Paper made from mechanical, semichemical or chemical pulps can be coated with alkali metal silicates with improvement in their colour if sufficient bleaching agent is added to the silicate solution to counteract its staining tendency. The viscosity of the silicate solution must be 1·0–50·0 centripoises at 20°C., the silicate should have alkali metal oxide : SiO_2 :: 1 : 1·6–4·0, the solution should contain 8–40% solids and have gravity 10–33·5° Bé. for alkali : silica ratio of 1:4 and 17–55° Bé. for a ratio of 1:1·6. C. O. C.

Transfer Sheets for Use with a Receiving Sheet Sensitised by a Colour-reactant Substance. National Cash Register Co. *BP* 712,216

The receiving sheet is sensitised with a colour-reactant substance, e.g. sodium zeolite in which the sodium may have been replaced by the ions of H, Ni, Cu, Fe, Zn, Hg, Ba, Pb, Cd or K. The transfer sheet is coated with a composition including a low-polarity hydrophobic wax and a hydrophobic oil containing a substance giving a distinctive colour when brought into contact with the colour reactant substance on the receiving sheet, e.g. a mixture of Crystal Violet lactone [3:3-bis-(*p*-dimethylaminophenyl)-6-dimethylaminophthalide] and benzoyl leuco methylene base



The first yields a dark blue immediately but this is not of good fastness to light and air, whereas the other yields a dark blue slowly which has good fastness to light and air. C. O. C.

Migratory Transfer of a Photographic Image during Development. Ozalid Co. *BP* 713,163

Cellulose Nitrate Lacquers, etc. (V p. 465).

Non-smudging Ink for Carbon or other Transfer Papers (V p. 465).

Theory of Dyeing of Paper (VIII p. 472).

XII—LEATHER; FURS; OTHER PROTEIN MATERIALS

Structure for Collagen. F. H. C. Crick. *J. Chem. Phys.*, **22**, 347–8 (1954): *Chem. Abs.*, **48**, 7085 (25 June 1954).

A suggested structure consists of two polypeptide chains helically wound around a common axis. The backbones of these chains are related by a diad coinciding with the fibre axis. The asymmetric unit consists of two residues, A and B. All the peptide links have the *cis*-configuration. The planes of successive peptide links on either chain are alternately perpendicular and approximately parallel to the fibre axis. The two chains are held together by hydrogen bonds perpendicular to the fibre axis and passing very close to it. The model imposes certain restrictions on the side chains. Residues of type B cannot be proline or hydroxy proline; those of type A can be. There is close approach between the β C atom of a residue of type B on one chain and that of the nearest residue of type A on the other chain, which suggests that one member of any such pair will be glycine. C. O. C.

Vegetable Tannage by Means of Modified Collagens and Polyamides. K. H. Gustavson. *J. Soc. Leather Trades Chem.*, **38**, 162–172 (May 1954).

Tannin fixation on collagen, methylated collagen, and a polyamide prepared from adipic acid–hexamethylenediamine salt (60%) and caprolactam (40%) is studied. J. W. B.

Glyoxal–Collagen Reaction as it contributes to Cross-linking. G. M. Sleichter and R. M. Lollar. *J. Amer. Leather Chem. Assocn.*, **49**, 414–422 (June 1954).

Load–extension studies on kangaroo-tail tendons treated with glyoxal indicate that chemical cross-linking has occurred. Its nature and points of attachment are not studied. J. W. B.

Thermoelectric Potentials of Dye–Gelatin Phosphors. L. Gombay. *Kolloid Z.*, **133**, 40–44 (Oct. 1953).

The thermoelectric potentials of gelatin dyed with Rhodulin Orange N have been measured at different temperatures and humidities. The dry phosphor gave the highest potential and the strongest phosphorescence. From the sign of the potential and the asymmetric conductivity, dyed gelatin phosphors must be classed as semi-conductors. L. P.

New Observations on the Chemistry of *N*-Carboxy-α-amino Acid Residues. D. G. H. Ballard, C. H. Bamford, and F. J. Weymouth. *Nature*, **174**, 173–175 (24 July 1954).

The polymerisation of many *N*-carboxy-α-amino acid anhydrides in highly polar organic liquids is catalysed by soluble anhydrous inorganic salts such as LiCl and NaI. The main products are cyclic polypeptides and derivatives of hydantoin-3-acetic acid. Kinetic studies of LiCl-catalysed reactions of glycine *N*-carbonic anhydride show that the initial rate of reaction is not significantly affected by water and does not depend on the method used for purifying the salt. Acids have a strong inhibitory effect, a trace present initially producing an induction period. The hydantoin-3-acetic acid is a comparatively strong acid and the reaction is self-inhibiting at quite small conversions. At salt concn. $>$ 0·1N. the rate shows second-order dependence on monomer concn. and is independent of LiCl concn. The rate falls off with decreasing concn. of LiCl below ca. 0·1N. The catalytic effect of salts is apparently connected with the presence of an $\rangle$NH group in the *N*-carbonic anhydride molecule and is attributed to complex formation between the anhydride, or hydantoin, and cation, resulting in the displacement of a proton and the formation of a molecule in which the N atom has basic properties sufficient for reaction with *N*-carboxy-α-amino acid anhydrides. *N*-Carboxy-α-amino acid anhydrides which are not *N*-substituted react readily in the presence of tertiary bases. The products contain considerable amounts of hydantoin-3-acetic acid derivatives and cyclic peptides. A high polarity of solvent favours hydantoin formation. The results obtained with tertiary bases thus resemble those with Li salts in polar media, and a similar mechanism is postulated. W. R. M.

Copolymerisation of *N*-Carboxyanhydrides and Amino Acids. W. Lautsch, R. Schütze, and W. Broser. *Kolloid Z.*, **133**, 1–4 (Oct. 1953).

The kinetics of polycondensation of mixtures of the *N*-carboxyanhydride of L-glutamic acid and DL- or D-phenylalanine in different proportions has been followed polarimetrically. L. P.

PATENTS

Deliming Hides and Skins. Joh. A. Benckiser. *BP* 714,165

The unrefined citric acid fermentation liquor obtained by fermenting carbohydrate compounds, e.g. with moulds, is cheap and has an excellent deliming effect without causing swelling. C. O. C.

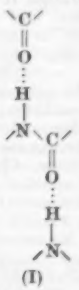
Mechanism of Leather Dyeing (VIII p. 472).

XIII—RUBBER; RESINS; PLASTICS

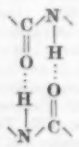
Microflora of Crêpe Rubber. J. N. Turner and M. E. Kennedy. *Nature*, **173**, 506 (13 March 1954).

Investigation of the Physical Structure of Synthetic Polyamides with the aid of Infrared Absorption Spectra. D. N. Shigorin, N. V. Mikhailov, and S. P. Makar'eva. *Doklady Akad. Nauk S.S.S.R.*, **94**, 717–720 (1 Feb. 1954).

Further infrared absorption measurements (see J.S.D.C., **69**, 227 (1953)) are made on polycaprolactam in the form of films (produced by various methods and varying in degree of crystallinity and other properties), and in the molten and dissolved states; and a further discussion is given of the significance of the positions and intensities of the fundamental absorption bands and their overtones. A band at ~ 3300 cm.$^{-1}$ is present at substantially const. intensity in all cases, though it varies somewhat in position; it is evidently associated with bonding that is thermodynamically advantageous under all conditions, and it is attributed to hydrogen bonds of type I, which are synergic with the general dipole interactions of the molecules. The intensities of bands observed in films at ~ 3080 and ~ 3210 cm.$^{-1}$ depend greatly on the conditions under which the films are prepared. Their intensities in the melt are low, and the bands disappear altogether when the polymer is dissolved in a polar solvent ("dichlorohydrin"). They are to be attributed to various types of intramolecular hydrogen bonds associated with folding of the chain, and also to intermolecular bonding of type II, which reduces the total dipole interaction.



(I)



(II)

A. E. S.

Investigation by the Ultracentrifuge Sedimentation Method of the Molecular Weight Distribution Function of Polyamides—I and II. S. E. Bresler, V. V. Korshak, S. A. Pavlova, and P. A. Finogenov. *Izvestiya Akad. Nauk S.S.S.R. Otdel. khim. nauk*, 344–353, 354–361 (March–April 1954).

A full discussion, with full experimental details, of work already reported briefly (see J.S.D.C., **69**, 227 (1953)). A. E. S.

Cation-exchange Materials from Cotton and Polyvinyl Phosphate. G. C. Daul, J. D. Reid, and R. M. Reinhardt. *Ind. Eng. Chem.*, **46**, 1042–1045 (May 1954).

Insoluble polyvinyl phosphate, prepared from polyvinyl alcohol and phosphorus oxychloride, is an effective cation-exchange resin with a capacity equivalent to those of commercial products. A soluble polyvinyl phosphate is prepared from polyvinyl alcohol and urea phosphate. When cotton is impregnated with its solution, dried, and baked, a high-capacity cation-exchange material is obtained. For the same loss of strength, four times as much phosphorus can be fixed to cotton by this method as with the usual urea phosphate treatment. W. K. R.

Interaction between Synthetic Polymers and Detergents. S. Saito. *Kolloid Z.*, **133**, 12–16 (Oct. 1953).

The effect of anion-active, cation-active, and non-ionic detergents on the viscosity of suspensions of polyvinyl alcohol or acetate has been studied. Time effects are shown to occur, and $\eta_{sp.}$–c_p curves are given for varying detergent amounts, where c_p is the polymer concentration. L. P.

PATENTS

Rubber Antioxidants. ICI. *BP* 714,072

Normal and basic Al, Ba, Ca, Mg, Sr and Zn salts of *aa-bis*-(2-hydroxy-3:5-diethylphenyl)alkanes are rubber antioxidants which are effective both before and after vulcanisation. C. O. C.

Plasticisers for Vinylidene Chloride Polymers. Distillers Co. *BP* 713,010

Dimethyl phthalate and dimethyltetrachlorophthalate are excellent plasticisers for vinylidene chloride polymers and copolymers. The plasticised polymers have good fastness to light. C. O. C.

Salt Solutions of Polyacrylonitrile. Dow Chemical Co. *USP* 2,648,646

Polymers containing $\leqslant 85\%$ of acrylonitrile dissolve at moderate temperatures in an aqueous solution containing $\leqslant 30\%$ of a solvent salt and 5–25% of a non-solvent salt, the total salt concentration being $\leqslant 55\%$. A complete list of cations and anions in the approximate order of their effectiveness in dissolving polyacrylonitrile is given. C. O. C.

Solvents for Polyacrylonitrile. Koppers Co. *USP* 2,648,653

Carbonates of formula $(CH_3)_2N{\cdot}COOCH_2R$ (R = H, CH_3, NO_2, OCN, SCN, nitromethyl, cyanomethyl and thiocyanomethyl) are good solvents for polyacrylonitrile. C. O. C.

Nacreous Polymethacrylic Ester Resins by Use of Pearl Essence. J. P. Ballbe. *BP* 712,433

A pure neutral and water white methacrylic ester is polymerised in presence of pearl essence. C. O. C.

Pearlescent Plastic Articles. Swedish Crucible Co. *USP* 2,648,098

A method of moulding pearlescent plastics to produce articles having a variegated pearlescent appearance throughout and free from tendency to split apart in layers. C. O. C.

Polymethacrylate Ester Coatings (V p. 465).
Removing Salts from Polyacrylonitrile (VI p. 469).

XIV—ANALYSIS; TESTING; APPARATUS

Filter-paper Chromatographic Analyses of Phosphate Mixtures. J. P. Crowther. *Nature*, **173**, 486 (13 March 1954).

Mixtures containing any or all of the following phosphates—ortho, pyro, tri, trimeta, and tetrameta—are separated into bands by filter-paper chromatography using *tert.*-butanol–water–formic acid (80 : 20 : 5). The blue phosphomolybdate colour is developed by ultraviolet irradiation, and the amount of P in each band is determined, with a standard deviation of 0·8, by a modification of the method of Boltz and Mellon (references are given). Components containing > 4 P per mol. remain on the starting line and are not resolved. The separation of phosphate mixtures of components with 1–9 P per mol. can be effected chromatographically using *n*-propanol–water–0·88 NH_4OH (60 : 20 : 20), but the resolution is not as clearly defined as with the former procedure. J. W. D.

Determination of Triphosphate and Pyrophosphate by Isotope Dilution. O. T. Quimby, A. J. Mabis, and H. W. Lampe. *Anal. Chem.*, **26**, 661–667 (April 1954).

Titrimetric Method for Total Phosphoric Anhydride. J. T. R. Andrews. *J. Amer. Oil Chem. Soc.*, **31**, 192–195 (May 1954).

A method is presented for the determination of phosphates which has been used in the analysis of phosphate-built synthetic detergents. The alcohol-insoluble portion of the detergent is ignited in a muffle furnace to remove volatile combustible matter, acidified with conc. HCl, evaporated to dryness, and reacidified, all the phosphate being converted to orthophosphoric acid. It is titrated with standard NaOH between pH 4·3 and 8·8 using a pH-meter. The standard deviation on samples of built synthetic detergents, in the range from 25% to 30% total P_2O_5 has been found to be 0·32. The method offers a considerable reduction in time compared with procedures involving precipitation of phosphomolybdate. P. G. M.

Use of Adsorption Columns in the Analysis of Soap and Detergent-stabilised Emulsions. R. P. Harker, J. M. Heaps, and J. L. Horner. *Nature*, **173**, 634–635 (3 April 1954).

Soap soln. and emulsions give, when passed through a column of ZeoKarb 225 (Permutit) mixed with powdered animal charcoal, clear soln. from which all organic matter has been removed. The charcoal diminishes the rate of percolation and increases the extent of adsorption; the reason for this is not known. With pure soaps over the concn. range 0·05–0·4%, elution with ethanol gives 98–100% recovery of the fatty acids. The components of an emulsion of purified, acid-free lanolin may be quant. separated, the soap fatty acids being eluted with ethanol, and the lanolin subsequently with trichloroethylene. Sodium cetyl sulphate is strongly held on the column, but may be eluted with ethylene glycol and subsequently titrated with NaOH. Lanolin emulsions stabilised with sodium cetyl sulphate may be resolved similarly using ethylene glycol and trichloroethylene in turn. J. W. D.

Semimicrodetermination of Hydroxyl Group in Long-chain Alcohols. R. T. Blickenstaff, J. R. Schaeffer, and G. G. Kathman. *Anal. Chem.*, **26**, 746–748 (April 1954).

The alcohol is sulphated with chlorosulphonic acid, and the mixture is neutralised, and titrated with cetyltrimethylammonium bromide; methylene blue is used as indicator. Alcohols of chain-length $> C_4$ do not interfere. Experimental details are given fully. J. W. D.

Determination of Protein-bound Carbohydrates by the Anthrone Reaction—Effect of Tryptophan. E. F. Tuller and N. R. Keiding. *Anal. Chem.*, **26**, 875–878 (May 1954).

The main absorption peak due to the carbohydrate–anthrone complex, at which measurement is made, is at 630 mμ. A secondary peak at 530 mμ. has been shown to be due to the formation of a tryptophan–sugar complex in the presence of excess anthrone and H_2SO_4. Interference due to this secondary peak may lead to a 5–15% error in the determination of carbohydrates in protein soln. when tryptophan is present, and in order to eliminate this a nomogram may be used which is prepared by plotting the ratio of the absorbances of the 530 mμ. peak to the 630 mμ. peak of the spectrum of known mixtures against the absorbance of the 630 mμ. peak. All experimental details are given, the nomogram is reproduced, and the results of trial analyses are presented and discussed. J. W. D.

Spray Reagent for the Detection of Carbohydrates. R. U. Lemieux and H. F. Bauer. *Anal. Chem.*, **26**, 920–921 (May 1954).

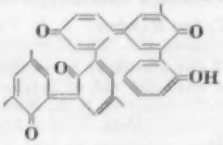
The chromatogram is sprayed with a slightly alk. (pH 7·2) soln. of IO_4^- and MnO_4^-; after development, the paper is washed with water to give a permanent record, on which the carbohydrates appear as brown spots on an almost white background. The sensitivity compares favourably with that of many other reagents in common use. J. W. D.

Three-level Capillary Viscometer for Study of Non-Newtonian Flow in Sealed Systems. J. G. Honig and C. R. Singleterry. *Anal. Chem.*, **26**, 677–680 (April 1954).

Liquid is released from a small bulb at the top of the instrument by lifting a small steel ball valve magnetically, and passes through capillaries separated by three measuring bulbs having volumes which vary in the ratio 4 : 2 : 1 from top to bottom, designed to secure approx. equal flow times for each bulb with a Newtonian liquid. The instrument, which is fully described and illustrated, allows repeated measurements to be made on a given soln., and yields reproducible results over a 250-fold viscosity range. The quant. characterisation of non-Newtonian flow by means of two constants derived from results obtained with the instrument is described. J. W. D.

Cerium (IV) Sulphate Oxidation of Phenols. W. R. Spencer and F. R. Duke. *Anal. Chem.*, **26**, 919–920 (May 1954).

Cerium (IV) sulphate may under suitable conditions be used to determine phenols either gravimetrically or volumetrically; it is highly specific in its removal of H atoms without simultaneous oxygenation. Full details of the procedure are given. There is evidence that the pptn. process is accompanied by polymerisation of the oxidation product, yielding a structure of the following type—



When a large excess of phenol is used, *oo'*-dihydroxydiphenyl may be isolated. J. W. D.

Aromatic Diazo Compounds. XVI—Determination of 2-Amino-5-naphthol-7-sulphonic Acid (J Acid). M. Matrka, J. Sova, and Z. J. Allan. *Chem. Listy*, **48**, 417–420 (1954): *Chem. Abs.*, **48**, 7495 (10 July 1954).

The J acid (0·006 mole in 5 ml. 2·5N.–Na_2CO_3) is coupled with diazotised *p*-$NO_2C_6H_4NH_2$ (0·1N.) in 150 ml. saturated soln. of Na xylenesulphonate and 10 ml. 2·5 N-HCl at 5°C. If coupling is done in aq. soln. the mixture is diluted with water, treated with ammonia, and chromatographied on paper with 20% ammonia. Presence of γ-acid is indicated by a characteristic violet spot. C. O. C.

Chromatography of Butter and Cheese Dyes and Dyes for Other Dairy Products. P. Jax and H. Aust. *Milchwiss. Ber.*, 145–189 (1953): *Chem. Abs.*, **48**, 7218 (25 June 1954).

The chromatographic behaviour of carotene mixture, bixin, Butter Yellow, Oil Yellow 2G, Cerise Yellow 3G, Sudan Red G, Cerise Orange G, Chrysoidine R, Cerise Red BB, Cerise Red G, Cerise Orange R and Martius Yellow in benzene, petroleum ether, and acetone with alumina, magnesia and franconite as adsorbents are described, and on paper chromatography using 80% methanol, 80% *iso*propylalcohol, methylalcohol–acetic acid–water (40 : 40 : 20) and *iso*butylalcohol–2N.-acetic acid–glycerine (160 : 30 : 10). In addition behaviour in acetone and in methylalcohol in column chromatography with alumina, magnesium and franconite is described of norbixin, Tartrazine, Fast Yellow, Chrysoin SGX, Chromotrope FB, Fast Red E, Naphthol Red S, New Coccin, Ponceau 6R, Tropeolin O, Tropeolin OO, Tropeolin 0001, Sudan III, Scarlet GN, Yellow 27175N, Orange GGN, Quinoline Yellow, Erythrosin, Naphthol Yellow S, Auramines, Alizarin Yellow R and Orange G. Paper chromatography in 80% *iso*propyl alcohol and in *iso*propyl alcohol–acetic acid–water (60 : 20 : 20) was carried out on the second group of dyes and both groups were tested with Carr–Price reagent (23% soln. of $SnCl_2$ in $CHCl_3$). Procedures are described, based on these behaviours, for separating and identifying mixtures of fat-soluble and water-soluble dyes alone or in butter or cheese. C. O. C.

Analytical Problems in the Determination of Evans Blue caused by Adsorption on Glass and Protein Surfaces. W. O. Caster, A. B. Simon, and W. D. Armstrong. *Anal. Chem.*, **26**, 713–715 (April 1954).

When Evans Blue (Tolidine–1824) is used to determine plasma volume spectrophotometrically, low results frequently obtain. The dye is strongly adsorbed on to the surface of the glass cell, and 20–50% may be lost in this way (or even more under certain conditions of pH and salt concn.). There is also strong adsorption on to the

surface of any protein which may be present. These errors are eliminated by the use of high concn. of Zephiran (an alkyldimethylbenzylammonium chloride), which removes the dye from the protein surface and prevents its adsorption on to glass. J. W. D.

Applications of Statistical Methods to Exposure Trials. II—Design of Exposure Tests. H. R. Touchin. *J. Oil & Col. Chem. Assocn.*, **37**, 248–263 (May 1954).

The types and sources of errors inherent in exposure trials are briefly discussed, and some standard experimental designs are described, illustrating how the influence of these errors on the experimental results may be minimised by their use. The basic designs considered are randomised-block, factorial, and split-plot designs, which are all amenable to statistical analysis. The number of replicate panels, the use of controls, and the combining of data from experiments conducted at different times and at different sites, are discussed briefly. The general advantages of these procedures are cited, and it is emphasised that voluminous data are not essential to statistical treatments. J. W. D.

Improved Strain Gauge for Precise Force Measurement in Single Fibres. W. J. Thorsen. *Text. Research J.*, **24**, 407–413 (May 1954).

An unbonded resistance-wire strain gauge is described that is sensitive to small forces, has high precision and accuracy, and is simple to construct. The low inertia and the high stability of this gauge make it especially suitable for the precise measurement of stress relaxation in single textile fibres over periods lasting from milliseconds to two months or more. A. B.

Static Electrification of Filaments. S. P. Hersh, E. P. Sharman, and D. J. Montgomery. *Text. Research J.*, **24**, 426–427 (May 1954).

A method for measuring static electricity using small areas of contact is described. Various metals and fibres have been investigated by this method, and preliminary results are given. A. B.

Determination of Total Sulphur in Viscose. B. Philipp. *Faserforsch. und Textiltech.*, **5**, 210–211 (May 1954).

The commonly used method of determining total S in viscose by oxidation with H_2O_2 and determination of the change in alkali content (= H_2SO_4 formed) gives results $\sim 16\%$ too high, owing, it is considered, to attack on the cellulose with formation of COOH groups. Satisfactory methods are (1) oxidation with hypobromite and gravimetric determination of sulphate formed, and (2) decomp. with acid and conversion of H_2S and CS_2 formed into CdS and K ethylxanthate respectively, which are estimated iodometrically. A. E. S.

New Method for Differentiation of Skin and Core of a Rayon Filament. W. R. Berry. *Text. Research J.*, **24**, 397–399 (May 1954).

A technique for staining the skin of a rayon filament and hence for determining the skin area is described. The core of the viscose rayon filament is first stained with Solophenyl Fast Blue Green BL (Gy). Gentian Violet is then added, when the blue-green dye is removed from the core and the skin is stained violet. A. B.

Solvent Etching of Cellulose Acetate Specimens for Electron Microscopy. V. Peck and W. Kaye. *Text. Research J.*, **24**, 295–300 (April 1954).

A technique is presented for etching cellulose acetate fibres and films by direct solution of the surface molecules. A relatively undisturbed interior layer of polymer is uncovered for replication. A. B.

Application of Electron Microscopy to the Study of Cellulose Acetate Fibres. V. Peck and W. Kaye. *Text. Research J.*, **24**, 300–306 (April 1954).

The application of electron microscopy to the study of cellulose acetate fibres has been demonstrated by the use of high-resolution Al–Be replicas. Abraded surfaces and the skin of fibres have been studied. A. B.

Detection of Modification in Animal Fibres. II—Tensile Recovery at 65% R.H. H. M. Burte. *Text. Research J.*, **24**, 414–422 (May 1954).

Methods are described for measuring parameters of the tensile recovery of animal fibres. The effect of crimp on these measurements is discussed, and also fibre-to-fibre variations. The effects of various chemical treatments are detailed. A. B.

Detection of Modification in Animal Fibres. III—Tensile Recovery in Water. H. M. Burte. *Text. Research J.*, **24**, 423–425 (May 1954).

The tensile recovery of animal fibres in water has been measured. The tensile recovery measured in water is shown to be much less sensitive for detecting chemical modification than the tensile recovery at 65% R.H. A. B.

Chromatographic Determination of Cystine as Cysteic Acid. E. Schram, S. Moore, and E. J. Bigwood. *Biochem. J.*, **57**, 33–37 (May 1954).

A method for the determination of the cystine plus cysteine content of proteins has been based upon oxidation of the protein by performic acid, hydrolysis by hydrochloric acid, and chromatographic determination of the resulting cysteic acid on columns of a base-exchange resin (Dowex-2). The method can be used directly on products in which a high carbohydrate content may render other methods inapplicable, or in cases where uncertainties which apply to the stability of cystine and cysteine even under favourable hydrolytic conditions may render an alternative method desirable. The procedure has been applied to the analysis of foods and purified proteins. P. G. M.

Identification of Dicarboxylic Acids in Polymeric Esters—Preparation and Properties of Diethyl Esters and Potassium Salts. R. W. Stafford, J. F. Shay, and R. J. Francel. *Anal. Chem.*, **26**, 656–661 (April 1954).

The diethyl esters of adipic, azelaic, citraconic, fumaric, itaconic, maleic, phthalic, and sebacic acids have been prepared and purified, and their physical properties determined. Mixtures can be resolved by distillation and/or ultraviolet and infrared spectroscopy. The salts are less suitable for the identification of the acids than are the esters. Full data are reported, and graphs and spectra are reproduced. J. W. D.

Testing the Serviceability of Goods after Repeated Laundering. O. Viertel. *Melliand Textilber.*, **35**, 541–544 (May 1954).

Methods of test are briefly discussed. Results using Weltzien's flexing abrasion tester (Knickscheuerprüfer; I) are compared with breaking strength (II). Good correlation is found, the former method being more sensitive to changes in degree of polymerisation in the cellulosic materials used. (I) does detect a difference in using a synthetic detergent instead of soap in repeated launderings, though II shows none. This difference is attributed to increased ash and lowered fat content obtained with synthetic detergents. H. E. N.

Propagation of Errors in Spectrophotometric Colorimetry. D. I. MacAdam. Spring Meeting of the Optical Society of America: *Anal. Chem.*, **26**, 786 (April 1954).

Errors of spectral reflectance, assumed to be equally uncertain at every wavelength, determine ellipsoids in tristimulus space. The chromaticity diagram can be interpreted as a plane in this space, and it intersects the ellipsoids of uncertainty in ellipses, all of the same shape and orientation. The axes of these ellipses $\propto$ their distances from the alchyne, divided by the luminous reflectance. These ellipses do not, however, represent uncertainties of chromaticities which, correctly determined (I. Nimeroff, *J. Opt. Soc. Amer.*, **43**, 531–533 (1953)), are represented by elliptical intersections of the chromaticity diagram with lines from the origin, tangential to the ellipsoids. In the constant-luminance diagram (D. L. MacAdam, *J. Opt. Soc. Amer.*, **43**, 536–538 (1953)) the ellipses of uncertainty have their axes all pointing toward ($U = W = 0$). The minor axes are equal in length to the diameters of the circles; the major axes are those diameters $\times (1 + r^2)^{\frac{1}{2}}$, where r is the distance of the ellipse from ($U = W = 0$, $V = 1$). For the case specified, the uncertainties of chromaticities cannot be represented by equal-sized circles in any plane; for that purpose a chromaticity diagram must be constructed on a surface of constant negative curvature which resembles a champagne glass. J. W. D.

Accurate Determination of Tristimulus Values with the Aid of a Retardation Plate. E. Allen. Spring Meeting of the Optical Society of America: *Anal. Chem.*, **26**, 786 (April 1954).

One of the biggest difficulties in determining tristimulus values from curves run on a recording spectrophotometer is the wavelength calibration. When hand integration is used, the wavelength scale is ordinarily established with the help of a correction curve derived from the didymium peaks. This procedure not only is tedious but may lead to loss of precision because of the necessity for interpolation between adjacent grid lines. A retardation plate (G. L. Bue and E. I. Stearns, *J. Opt. Soc. Amer.*, **35**, 465 (1945)) can be used for constructing a wavelength grid by setting the pen at a max. or a min. of the transmittance curve of the plate and then allowing the pen to travel up and down the paper. Because of the sharpness of the peaks, this grid can be drawn very accurately, and makes available ca. 55 ordinates for integration of spectrophotometric curves. The curve, plotted on transparent paper, is aligned over the grid, and the reflectance or transmittance for each of the wavelengths can be read with considerable precision. Each value is then multiplied by an appropriate factor, and the products are summed to give the tristimulus value. The procedure is thus similar to the weighted-ordinate method of integration, except that readings are taken at the retardation-plate wavelengths instead of at every 10 mμ. The weights to be applied are calc. for the retardation-plate wavelengths from a table of running sums. Since errors of paper positioning and irregularity in the wavelength cam will not affect the results by the proposed method, much greater accuracy should be obtained. The proposed procedure is also more convenient, since no wavelength correction or interpolation is required. J. W. D.

Use of Charts for Rapid Calculation of Colour Differences. H. R. Davidson and J. J. Hanlon. Spring Meeting of the Optical Society of America: *Anal. Chem.*, **26**, 787 (April 1954).

Previously reported methods of using MacAdam visual-sensitivity ellipses (references are given) for the evaluation of surface colour differences lack speed and simplicity. A series of charts have been prepared which are based on the MacAdam ellipses and the data of Davidson and Friede (*J. Opt. Soc. Amer.*, **43**, 581 (1953)). As suggested by MacAdam (*ibid.*, **33**, 18 (1943)) Δx and Δy are plotted directly on the appropriate non-Cartesian uniform-chromaticity chart; the chromaticity difference is then read as a linear distance from the origin, and is plotted against ΔY on a second chart. The linear distance of the point from the origin in the second chart is a direct measure of the colour difference. Colour tolerances for production control are represented in both diagrams by circles rather than ellipses. J. W. D.

Colorimetric Calibration of Colorant Systems. H. R. Davidson and H. Hemmendinger. Spring Meeting of the Optical Society of America: *Anal. Chem.*, **26**, 787 (April 1954).

If a set of colorants is to be used in making large numbers of specified colours, a calibration of the relationship between colorant composition and colorimetric specifications provides a very efficient means of procedure. A set of six chromatic paints plus black and white was chosen on the basis of colour gamut, fastness, and other physical properties; since mixtures of the two chromatic paints plus black and white provide three degrees of freedom, such mixtures are sufficient to obtain any colour within the gamut of the chosen paints. The required calibration must therefore relate the ratios of chromatic paints, black, and white to colorimetric specifications within the gamut. This calibration was made by painting samples of a constant-ratio type of colorant mixture system, determining the C.I.E. and Munsell specifications, and then establishing graphs of the relation between colorant ratios and colorant co-ordinates. The mixture formulae for the desired Munsell renotation samples were then read from these graphs. Although the project involved the use of paints, the same principles may be applied to other types of colorant. J. W. D.

Measurement in the Infrared. K. Hoffmann. *Melliand Textilber.*, **35**, 285–286 (March), 396–399 (April 1954).

The measurement of infrared absorption is best carried out using a spectrophotometer. Measurement by the following methods is discussed in detail— (1) Spectacles which transmit only >700 mμ., when the observer becomes sensitive only to 700–760 mμ. with a maximum at 720 mμ. (2) Photographically, usually not beyond 850–900 mμ. using Kodak Emulsion IR–ER with Wratten Filter 89. (3) A new electrical apparatus in which the scene is focussed on to a photocathode, sensitive up to 1200 mμ. The latter emits electrons depending on the intensity of illumination, and these are made visible by means of a screen. This instrument can be used to observe people by infrared illumination in apparent darkness, i.e. without their knowledge. (4) Further in the infrared, use is made of semi-conductors, e.g. PbS, PbSe. H. E. N.

Determination of the Crystallinity and Melting Point of Polyethylene from Infrared Absorption Measurements. V. N. Nikitin and E. I. Pokrovskiĭ. *Doklady Akad. Nauk S.S.S.R.*, **95**, 109–110 (1 March 1954).

The authors have previously established that the intensity of the absorption band at 1308 cm.$^{-1}$, observed for polyethylene and higher alkanes, may be taken as a measure of the amorphous character of the substance; it is absent in perfectly crystalline hydrocarbons. Observations on a sample of polyethylene at various temperatures show that for this band the transmission–temp. curve consists of three linear portions joined by smooth curves; the linear sections, when produced, intersect at 50°c. and 111°c., the temperatures of incipient and complete melting respectively (practically identical values are given by the dilatometric method). The proportion of amorphous phase in the polyethylene is considered to be directly proportional to the optical density, the melt being regarded as 100% amorphous. This quantity, and hence the crystallinity, can therefore be readily determined at any given temp. (the sample examined is 56·6% crystalline at 20°c.). A. E. S.

PATENTS

Apparatus for Determining Particle Size Distribution. Simon–Carves. *BP* 712,434

A settling tube receives a suspension of the finely divided material in a non-solvent. The lower end of the tube is open and can be immersed in a large volume of the non-solvent. Under this lower end there is a receiver for settled particles and means for recording their total weight. C. O. C.

Comparator for Assisting in Identification of Unknown Stains, Pigments, Paints, etc. G. A. Yale. *USP* 2,647,433

A unitary device, devised in the first place for use by dryceleaners, which enables rapid and accurate comparison of an unknown stain upon fabric with a number of prepared standards under varying lighting conditions. For this purpose 75–150 standards are normally needed and the device stores them so that any one of them is instantly accessible for comparison with the unknown stain. C. O. C.

Determining the Shrinking Temperature of Leather, Hides, Skins and the like. K. Wachtel. *BP* 714,111

A strip of the leather is supported under slight tension within a liquid which can be heated. There is a maximum thermometer in the liquid, and a solenoid-operated valve or switch for controlling the heat. A device connected to the strip breaks the control current of the solenoid immediately the strip commences to shrink and so cuts off the supply of heat. C. O. C.

Substituted Benzidines and Related Compounds as Reagents in Analytical Chemistry. XIII — Behaviour of certain *N*- and *NN'*- Alkylated Benzidines towards Oxidising Agents (IV p. 458).
Chalking of Titanium Dioxide. Its Evaluation by the Mandelic Acid Paste Method (V p. 465).
Microscopy in Cellulose Research (VI p. 466).
Potential Dyeing Methods for Polyacrylonitrile Fibres (VIII p. 471).

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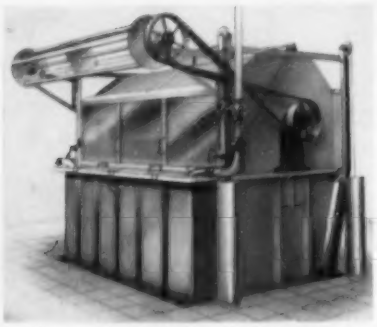

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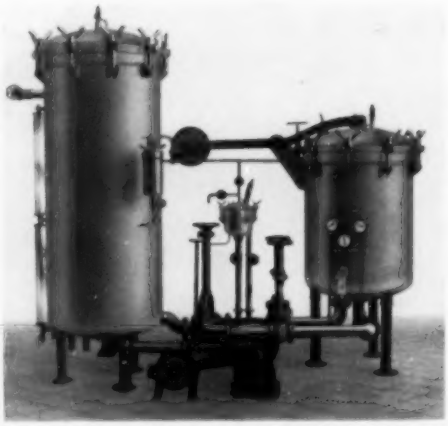

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FORTHCOMING MEETINGS OF THE SOCIETY — *continued from page* xii

Wednesday, 26th January 1955

MIDLANDS SECTION. *I do it this way*! Demonstrations of novel testing techniques by local members. College of Technology, **Leicester.** 7 p.m.

BRADFORD JUNIOR BRANCH. *Processing of "Dynel" Textiles.* D. H. Stott, Esq. (Gemec Chemical Company). **Bradford** Technical College. 7.15 p.m.

Friday, 28th January 1955

LONDON SECTION. Annual Dinner Dance at The Waldorf Hotel, **London W.C.2.**

Friday, 4th February 1955

LONDON SECTION. *Textile Performance Standards for the Distributor.* Messrs. F. Cowles and J. S. Ingham (Marks and Spencer Ltd.). Royal Society Rooms, Burlington House, **London W.1.** 6 p.m.

Tuesday, 8th February 1955

MANCHESTER SECTION. Joint meeting with the Textile Institute in Macclesfield. *The Dyeing Properties of "Terylene" Polyester Fibre.* J. G. Graham, Esq., B.Sc. Fuller details later.

Wednesday, 9th February 1955

NORTHERN IRELAND SECTION. *Fastnesses of Coloured Textiles as they Affect the General Public.* J. S. Ingham Esq. (Marks & Spencer Ltd.). Thompson's Restaurant, Donegall Place, **Belfast.** 7.30 p.m.

Tuesday, 15th February 1955

HUDDERSFIELD SECTION. *Non-Textile Uses of Dyestuffs.* J. P. Gill, Esq., B.Sc. (Imperial Chemical Industries Ltd.). Joint meeting with Huddersfield Section of the Royal Institute of Chemistry. The Co-operative Society Cafe, Buxton Road, **Huddersfield.** 7.30 p.m.

Friday, 18th February 1955

MANCHESTER SECTION. *The Soiling of Synthetic and Natural Fibres.* G. G. Taylor, Esq., B.Sc. Textile Institute. 6.30 p.m.

Monday, 21st February 1955

BRADFORD JUNIOR BRANCH. Messrs. I.C.I. Ltd. and Petroleum Film Bureau. Film Evening.

Wednesday, 23rd February 1955

MIDLANDS SECTION. *The Classification of Dyestuffs by their Dyeing Characteristics.* W. Beal, Esq., B.Sc. Kings Head Hotel, **Loughborough.** 7 p.m.

Friday, 25th February 1955

MANCHESTER SECTION. Annual Dance.

March 1955

LONDON SECTION. The London Lecture. Details later.

Friday, 4th March 1955

MIDLANDS SECTION. MIDLANDS SECTION DINNER. Kings Head Hotel, **Loughborough.** 7 p.m.

Wednesday, 9th March 1955

NORTHERN IRELAND SECTION. Film Evening. (Joint Meeting with Textile Institute). Thompson's Restaurant, Donegall Place, **Belfast.** 7.30 p.m.

Thursday, 10th March 1955

MIDLANDS SECTION. *The Diffusion of Vat Dyes into Cellulose.* R. H. Peters, Esq., Ph.D., F.S.D.C., and T. Watson, Esq., Ph.D. (Dr. Peters lecturing). Gas Theatre, **Nottingham.** 7 p.m.

Tuesday, 15th March 1955

HUDDERSFIELD SECTION. *Sulphur Colours for Special Purposes.* H. Senior, Esq. (James Robinson & Co. Ltd.). Preceded by Annual General Meeting, Princess Cafe, **Huddersfield.**

Thursday, 17th March 1955

BRADFORD JUNIOR BRANCH. *Dyeing and Finishing of Acetate Woven and Knitted Fabrics.* R. J. Mann, Esq., B.Sc. (British Celanese Ltd.). **Bradford** Technical College. 7.15 p.m.

Friday, 18th March 1955

MANCHESTER SECTION. One Day Symposium. Full details later.

Wednesday, 6th April 1955

MIDLANDS SECTION. Paper by G. H. Lister, Esq., B.Sc., Ph.D. (Subject later) (ANNUAL GENERAL MEETING at 6.30 p.m.). Kings Head Hotel, **Loughborough.**

Friday, 15th April 1955

MANCHESTER SECTION. Annual General Meeting. Full details later.

Thursday, 21st April 1955

MIDLANDS SECTION. *Some Experiences of a knitted-goods dyer.* A. W. Carpenter. (Joint Meeting with the Textile Institute Kidderminster Section). Carpet Trades Canteen, Mill Street, **Kidderminster.** 7 p.m.

MEMBERS' CHANGES OF ADDRESS

Ashby, W. L., formerly of Highleigh, Whaley Lane, Whaley Bridge, near Stockport, to Eccles Nook, Whitehough, Chinley, near Stockport

Baranek, R., formerly of 2 Chaucer Street, Chaucer Villas, Nottingham, to 134 Longford Road, Coventry

Crabtree, P. G., formerly of 19 Ravenstone Drive, Sale, Manchester, to 18 Leegate Gardens, Heaton Mersey, Stockport

Crane, G., formerly of "Caldy", Broadwater Avenue, Letchworth, to "Ashton", Willingdon-Park-Drive, Willingdon Estate, Eastbourne

Djanogly, P., formerly of 30 Westcotes Drive, Leicester, to 11 Alvanley Gardens, Hampstead, London NW6

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The Publications Committee is prepared to receive Advertisements relating to Situations Vacant, Situations Wanted, or Miscellaneous Items for insertion on this page of the Journal. Advertisements of Situations Wanted are gratis to individual members, but must not exceed twenty-four words in length.

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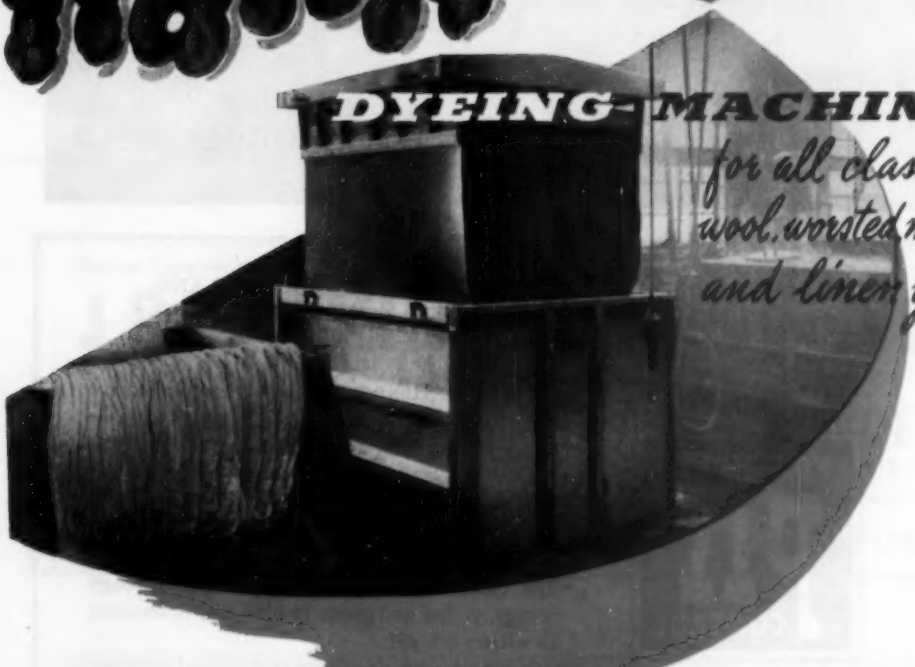

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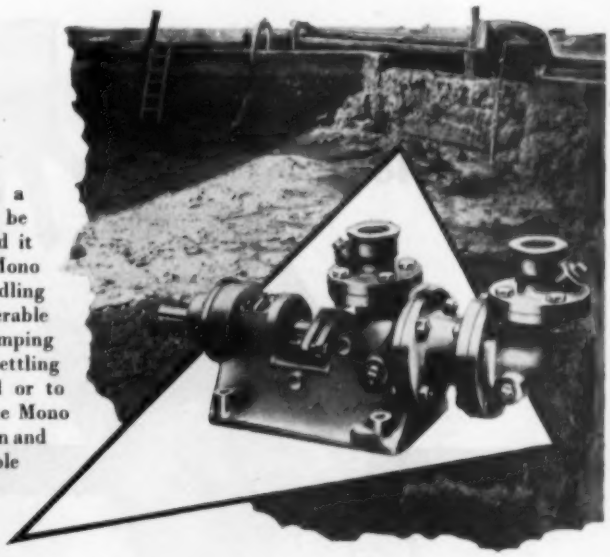

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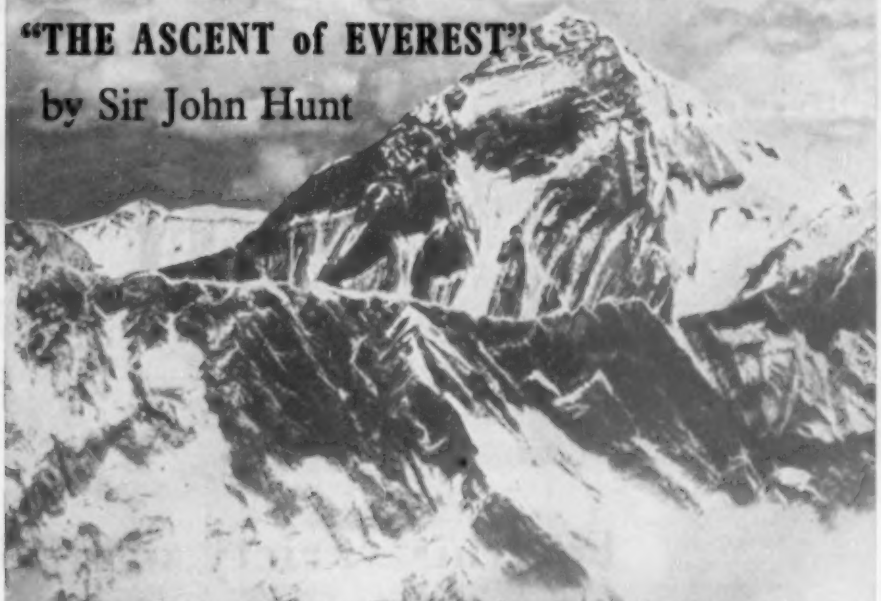

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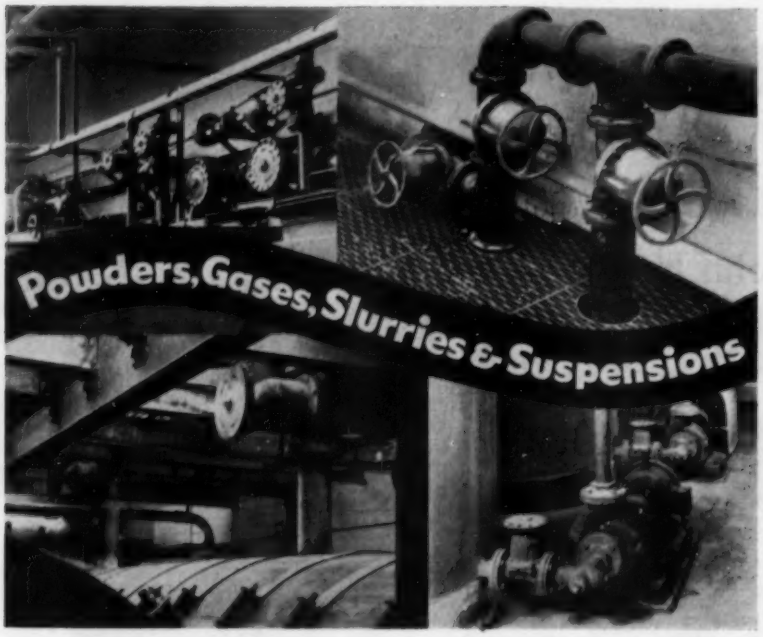

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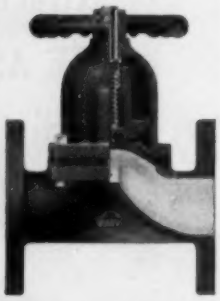

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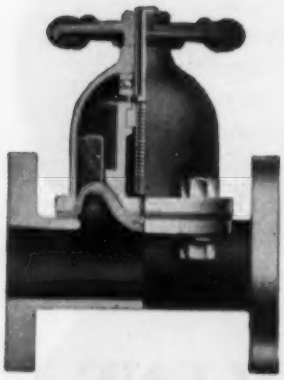

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Manuscripts submitted for publication in the *Journal* should be typewritten (double spacing) on good-quality paper, using one side of the paper only and leaving a margin at least 1 in. wide on the left-hand side. The time taken in refereeing papers (both lectures and communications) will be reduced to a minimum when authors submit two copies of the typescript.

In view of the high costs of publication, it is essential that authors should be as concise as possible. When experimental procedure has already been published, a literature reference to the paper containing the details is sufficient, whilst well known experimental methods should be described very briefly.

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The list of references should be given at the end of the manuscript and the abbreviations used should be, as far as possible, those given in the "List of Periodicals Abstracted" included at the end of the Index to the preceding year's *Journal*. Reference numbers in this list should be neither enclosed in brackets nor followed by full-stops. As far as possible throughout the manuscript the abbreviations listed in the Jan. 1950 issue (p. 54) should be used. Tables should be numbered consecutively in Roman numerals and Figures in Arabic numerals.

The number of figures and graphs should be kept as low as possible, and data should be presented in the form of either tables or graphs, not both. Drawings should be carefully prepared, preferably in Indian ink, on plain white drawing paper or, preferably, Bristol board. In graphs, the frame and actual curves should be ruled and inked more heavily than any co-ordinate lines, and the latter should not be close together as in ordinary graph paper. Experimental points should always be given, and where several graphs appear in a single Figure clear means of differentiation must be adopted. All numbers and legends are set up in type by the printer, and authors should therefore indicate them lightly in pencil.

Twenty-five free copies of a reprint are supplied to the author of an original paper published in the *Journal*, or fifty free copies are supplied when there are two or more authors, and a further number may be purchased from the Society at the rates given below.

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